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CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY

PAGE

I.—The Affinity Values of Tropine and its Derivatives. By Victor Herbert Veley 1

II.—The Formation and Reactions of Imino-compounds. Part VII. The Formation of 1:3-Naphthylenediamine from β-Imino-α-cyano-γ-phenylpropane. By Stanley Robert Best and Jocelyn Field Thorpe 8

III.—The Optical and Sensitising Properties of the *iso*Cyanine Dyes. By Samuel Edward Sheppard (1851 Exhibition Scholar) 15

IV.—Hydroaromatic Ketones. Part I. Synthesis of Trimethyl*cyclo*hexenone (*iso*Phorone) and Some Homologues. By Arthur William Crossley and Charles Gilling (Salters' Fellow) 19

V.—The Decomposition of Carbon Dioxide by the Silent Electric Discharge. By Alfred Holt, jun. 30

VI.—The Absorption Spectra of para-Benzoquinone, Quinol, and Quinhydrone in the State of Vapour and in Solution. By Walter Noel Hartley and Alfred Godfrey Gordon Leonard 34

VII.—The Constitution of para-Benzoquinone. By Walter Noel Hartley 52

VIII.—The Electrical Conductivity of Phosphoric Acid. By Harry Edward William Phillips, M.A., B.Sc. . . . 59

IX.—The Molecular Volumes of the Nitrites of Barium, Strontium, and Calcium. By Prafulla Chandra Rây . 66

X.—Organic Derivatives of Silicon. Part IX. Experiments on the Resolution of *dl*-Benzylethylpropyl*iso*butylsilicanesulphonic Acid. By Frederic Stanley Kipping and Harold Davies 69

XI.—Chemical Examination of Eriodictyon. Part II. By Frank Tutin and Hubert William Bentley Clewer . 81

XII.—The Slow Decomposition of Ammonium Chromate, Dichromate, and Trichromate by Heat. By Walter Craven Ball 88

XIII.—The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part III. By Arthur Slator and Douglas Frank Twiss 93

XIV.—The Crystallisation of Externally Compensated Mixtures. By Frederic Stanley Kipping and William Jackson Pope 103

PAGE

XV.—Formation of *cyclo*Hexanone Derivatives from Olefinic Compounds. By SIEGFRIED RUHEMANN 109

XVI.—The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids. Part II. By SIEGFRIED RUHEMANN 117

XVII.—The Hydration of Precipitates. By SPENCER UMFREVILLE PICKERING, M.A., F.R.S. 123

XVIII.—Chlorine Derivatives of Substituted Carbamides. By FREDERICK DANIEL CHATTAWAY and DONALD FREDERICK SANDYS WÜNSCH 129

XIX.—The Interaction of Hydrogen and Chlorine. By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON . 135

XX.—Nitrogen Chloride. By DAVID LEONARD CHAPMAN and LEONARD VODDEN 138

XXI.—The Relation between Absorption Spectra and Chemical Constitution. Part XIII. Some Pyrones and Allied Compounds. By EDWARD CHARLES CYRIL BALY, JOHN NORMAN COLLIE, and HERBERT EDMESTON WATSON 144

XXII.—Action of Alcohols on Metallic Calcium. By FREDERICK MOLLWO PERKIN and LIONEL PRATT 159

XXIII.—The Atmospheric Oxidation of β-Methylhydrindone. By ARTHUR H. SALWAY, Ph.D., B.Sc., and F. STANLEY KIPPING 166

XXIV.—The Condensation of Oxymethylenecamphor with Primary and Secondary Amino-compounds. By WILLIAM JACKSON POPE and JOHN READ 171

XXV.—The Triazo-group. Part VII. Interaction of Benzhydroximic Chloride and Sodium Azide. By MARTIN ONSLOW FORSTER 184

XXVI.—The Triazo-group. Part VIII. Azoimides of the Monobasic Aliphatic Acids. By MARTIN ONSLOW FORSTER and ROBERT MÜLLER 191

XXVII.—Nitro-derivatives of ortho-Xylene. By ARTHUR WILLIAM CROSSLEY and NORA RENOUF 202

XXVIII.—The Relation between the Chemical Constitution and Optical Properties of the Aromatic α- and γ-Diketones. By IDA SMEDLEY 218

XXIX.—Note on the Constitution of the Carboxyl Group. By IDA SMEDLEY 231

XXX.—A Synthesis of para-Urazine from Carbamide. By FREDERICK DANIEL CHATTAWAY 235

XXXI.—The Divergence of the Atomic Weights of the Lighter Elements from Whole Numbers. By ALFRED CHARLES GLYN EGERTON, B.Sc. 238

XXXII.—The Constituents of the Bark of Prunus serotina. Isolation of l-Mandelonitrile Glucoside. By FREDERICK BELDING POWER and CHARLES WATSON MOORE . . . 243

PAGE

XXXIII.—The Formation and Reactions of Imino-compounds. Part VIII. The Formation of Methyl Derivatives of 2-Phenyl-1:3-naphthylenediamine from the Three Tolylacetonitriles. By STANLEY ROBERT BEST and JOCELYN FIELD THORPE 261

XXXIV.—Formation of Heterocyclic Compounds. Part I. 1-Phenylpyrrolidine-2:5-dicarboxylic Acid from Adipic Acid. By HENRY RONDEL LE SUEUR 273

XXXV.—Derivatives of Naphthacenequinone. Part III. By DOROTHY HARROP, ROLAND VICTOR NORRIS, and CHARLES WEIZMANN 279

XXXVI.—Contributions to the Chemistry of the Terpenes. Part IV. The Oxidation of Pinene with Mercuric Acetate. By GEORGE GERALD HENDERSON and JAMES WATSON AGNEW 289

XXXVII.—The Relationship between the Constitution and the Absorption Spectra of Pyridine and Various Derivatives. By JOHN EDWARD PURVIS 294

XXXVIII.—Benzyl and Ethyl Derivatives of Silicon Tetrachloride. By GEOFFREY MARTIN and FREDERIC STANLEY KIPPING 302

XXXIX.—Esterification Constants of Substituted Acrylic Acids. Part III. By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS 315

XL.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIV. Ethyl Tartrate in Benzaldehyde and in Quinoline. By THOMAS STEWART PATTERSON and DAVID PATERSON MCDONALD, M.A., B.Sc. . 321

XLI.—The Action of β-Rays on Photosensitive Solutions. By OTTO FLASCHNER 327

XLII.—The Effect of Contiguous Unsaturated Groups on Optical Activity. Part I. By THOMAS PERCY HILDITCH (1851 Exhibition Scholar) 331

XLIII.—The Isolation of the Aromatic Sulphinic Acids. By JOHN THOMAS, B.Sc. 342

XLIV.—The Decomposition and Sublimation of Ammonium Nitrite. By PRAFULLA CHANDRA RÂY. 345

XLV.—Benzyl Sulphoxide: a Possible Example of Dynamic Isomerism. By JOHN ARMSTRONG SMYTHE 349

XLVI.—The Nature of Ammoniacal Copper Solutions. Part II. The Solubility of Cupric Hydroxide in Ammoniacal Sulphate Solutions. By HARRY MEDFORTH DAWSON . 370

XLVII.—Brazilin, Hæmatoxylin, and their Derivatives. Part X. The Constitution of Trimethylbrazilone, of α- and β-Anhydrotrimethylbrazilone, and of the corresponding Hæmatoxylin Derivatives. By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (1851 Exhibition Scholar) . 381

XLVIII.—A Study of Some Asymmetric Compounds. By FREDERIC STANLEY KIPPING 408

PAGE

XLIX.—The Action of Ethylene Dibromide on Monomethylaniline. By JOHN GUNNING MOORE DUNLOP and HUMPHREY OWEN JONES 416

L.—The Condensation of Dimethyldihydroresorcin with Ethylamine. By PAUL HAAS 421

LI.—An Interpretation of the Hantzsch-Werner Hypothesis. By MARTIN ONSLOW FORSTER and FREDERICK PERCY DUNN . 425

LII.—The Triazo-group. Part IX. Transformation of Cinnamoylazoimide into Cinnamenylcarbimide (Cinnamenyl *iso*Cyanate). By MARTIN ONSLOW FORSTER 433

LIII.—Note on the Detection of White or Ordinary Phosphorus in the Igniting Composition of Lucifer Matches. By THOMAS EDWARD THORPE, C.B., F.R.S. 440

LIV.—Salicylidene-*m*-toluidine, a New Phototropic Compound; Salicylideneamines: Salicylamides. By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD 441

LV.—The Atomic Volumes of Phosphorus. Part II. Phosphorus and Bromine. By EDMUND BRYDGES RUDHALL PRIDEAUX 445

LVI.—The Action of Ethyl Carbamate on Esters of Organic Acids and Mustard Oils. By SIEGFRIED RUHEMANN and JOHN GILLIES PRIESTLEY 449

LVII.—Analytical Investigation of Zirconium Metal. By E. WEDEKIND, Ph.D., and S. JUDD LEWIS, B.Sc., F.I.C. . 456

LVIII.—The Preparation of Dichlorocarbamide. By FREDERICK DANIEL CHATTAWAY 464

LIX.—The Alkaloids of Senecio latifolius. By HENRY EDGAR WATT, D.Sc. (Dunelm.) 466

LX.—Estimation of Primary, Secondary, and Tertiary Amines. Part I. By JOHN JOSEPH SUDBOROUGH and HAROLD HIBBERT 477

LXI.—The Condensation of Ketones and Aldehydes with the Sodium Derivative of Ethyl Cyanoacetate. By WALTER NORMAN HAWORTH 480

LXII.—The Action of fuming Sulphuric Acid on Triphenylsilicol. By FREDERICK STANLEY KIPPING and GEOFFREY MARTIN 489

LXIII.—Thiotetrahydroquinazolines, Methylenecarbamides, Dicarbanilinomethylenediamines and their Homologues. By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD . 494

LXIV.—Silicon Researches. Part XI. Silicotetrapyrrole. By J. EMERSON REYNOLDS 505

LXV.—Silicon Researches. Part XII. The action of Silicochloroform on Potassium Pyrrole. By J. EMERSON REYNOLDS 508

LXVI.—Silicon Researches. Part XIII. Silicon Halides and Pyridine, Acetonitrile, etc. By J. EMERSON REYNOLDS . 512

LXVII.—The Ignition-Temperatures of Gases. By HAROLD BAILY DIXON and HUBERT FRANK COWARD 514

PAGE

LXVIII.—Studies in Asymmetric Synthesis. Part VII. The Influence of the *d*-Amyl Group. By ALEX. MCKENZIE and HERMANN AUGUST MÜLLER. 544

LXIX.—Tetraketopiperazine. Part II. By ALFRED THEOPHILUS DE MOUILPIED and ALEXANDER RULE . . . 594

LXX.—The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part IV. Derivatives of Dihydroxyphenyl-acetic, -glycollic, and -glyoxylic Acids. By GEORGE BARGER and ARTHUR JAMES EWINS . . . 552

LXXI.—The Conversion of *d*-α-Methyl*iso*serine into *d*-α-Methylglyceric Acid. By FRANCIS WILLIAM KAY (1851 Exhibition Scholar of the University of Manchester) 560

LXXII.—A Polarimetric Method of Identifying Chitin. By JAMES COLQUHOUN IRVINE 564

LXXIII.—The Alkyl Compounds of Platinum. By WILLIAM JACKSON POPE and STANLEY JOHN PEACHEY. . . . 571

LXXIV.—Studies in the Azine Series. Part I. The Constitution of Safranine. By JOHN THEODORE HEWITT, SIDNEY HERBERT NEWMAN, and THOMAS FIELD WINMILL . 577

LXXV.—Condensations of Cyanohydrins. Part I. Condensation Products from Anisaldehydecyanohydrin and Cinnamaldehydecyanohydrin. By HAMILTON MCCOMBIE and ETHEL PARRY, M.Sc. (Priestley Research Scholar of the University of Birmingham) 584

LXXVI.—The Miscibility of Solids. By ERNEST VANSTONE, B.Sc. (Wales) ("Isaac Roberts" Research Scholar) . . . 509

LXXVII.—Some Esters of Antimony Trioxide. By JOHN FRANCES MACKEY 604

ANNUAL GENERAL MEETING 611

PRESIDENTIAL ADDRESS 624

LXXVIII.—Contributions to the Chemistry of Cholesterol and Coprosterol. By CHARLES DORÉE 638

LXXIX.—Iodine Dioxide. By MATTHEW MONCRIEFF PATTISON MUIR 656

LXXX.—*iso*Amygdalin and the Resolution of its Hepta-acetyl Derivative. By FRANK TUTIN 663

LXXXI.—The Miscibility of the Pyridine Bases with Water and the Influence of a Critical-solution Point on the Shape of the Melting-point Curve. By OTTO FLASCHNER . . 668

LXXXII.—The Formation and Reactions of Imino-compounds. Part IX. The Formation of Derivatives of *cyclo*Pentane from $\alpha\delta$-Dicyano-derivatives of Butane. By STANLEY ROBERT BEST and JOCELYN FIELD THORPE 685

LXXXIII.—Nitrosoacetylamino-derivatives of the Benzene and Diphenyl Series. By JOHN CANNELL CAIN 714

LXXXIV.—The Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule. By BERNHARD FLÜRSCHEIM 718

PAGE

LXXXV.—The Constituents of the Rhizome of Apocynum androsaemifolium. By CHARLES WATSON MOORE . . 734

LXXXVI.—A Crystalline Bleaching Powder. By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES . . 751

LXXXVII.—The Affinity Values of Certain Alkaloids. By VICTOR HERBERT VELEY 758

LXXXVIII.—Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules. By NORMAN LESLIE GEBHARD and HERBERT BRYAN THOMPSON. 767

LXXXIX.—Experiments on the Walden Inversion. Part II. The Interconversion of the Optically Active Mandelic Acids. By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH . . 777

XC.—Indican. Part II. By ARTHUR GEORGE PERKIN and FREDERICK THOMAS 793

XCI.—Studies of Dynamic Isomerism. Part VIII. The Relationship between Absorption Spectra and Isomeric Change. Absorption Spectra of Halogen, Nitro-, and Methyl Derivatives of Camphor. By THOMAS MARTIN LOWRY and CECIL HENRY DESCH 807

XCII.—Indican. Part III. By FREDERICK THOMAS, WILLIAM POPPLEWELL BLOXAM, and ARTHUR GEORGE PERKIN . . 824

XCIII.—Indoxylic Acid. By ARTHUR GEORGE PERKIN . . 847

XCIV.—The Distillation of Butter Fat, Cocoanut Oil, and their Fatty Acids. By KENNETH SOMERVILLE CALDWELL and WILLIAM HOLDSWORTH HURTLEY 853

XCV.—The Preparation and Properties of the *N*-Tribromo-substituted Hydrazines (the Diazonium Perbromides). By FREDERICK DANIEL CHATTAWAY 862

XCVI.—A Method for Investigating Dissociation Equilibria in Solutions, and its Application to the Study of Aqueous Potassium Mercuri-iodide Solutions. By HARRY MEDFORTH DAWSON 870

XCVII.—Solubility of Lead Sulphate in Concentrated Solutions of Sodium and Potassium Acetates. By JOHN JACOB FOX 878

XCVIII.—The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part II. Brilliant-green and Malachite-green. By NEVIL VINCENT SIDGWICK and TOM SIDNEY MOORE 889

XCIX.—The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part III. Diaminotriphenylcarbinol. By NEVIL VINCENT SIDGWICK and ALBERT CHERBURY DAVID RIVETT 899

C.—Labile Isomerism Among the Acylsalicylamide, Acylhydroxyamine, and Phenylbenzometoxazine Groups. By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS . 908

CI.—The Colour and Constitution of the Alkyl Iodides of Cyclic Bases. By CHARLES KENNETH TINKLER 921

PAGE

CII.—The Hydrolysis of Amygdalin by Emulsin. Part III. Synthesis of *d*-Benzaldehydecyanohydrin. By S. J. MANSON AULD, D.Sc. (Lond.), Ph.D. 927

CIII.—Substituted Dihydrobenzenes. Part III. The So-called 1:1-Dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene of Harries and Antoni. By ARTHUR WILLIAM CROSSLEY and NORA RENOUF . . . 930

CIV.—Affinity Constants of Hydroxy- and Alkyloxy-acids. By ALEXANDER FINDLAY, WILLIAM ERNEST STEPHEN TURNER, and GERTRUDE EMILY OWEN 938

CV.—Studies in the Camphane Series. Part XXVI. Aryl Derivatives of Iminocamphor. By MARTIN ONSLOW FORSTER and TOM THORNLEY 942

CVI.—The Colour of Aqueous Solutions of Violuric Acid. By FREDERICK GEORGE DONNAN and WILHELM SCHNEIDER, Ph.D. 956

CVII.—The Retarding Effect of Oxygen on the Rate of Interaction of Chlorine and Hydrogen. By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON . . . 959

CVIII.—An Examination of Irritant Woods. Part I. Chloroxylonine from the East Indian Satinwood. By S. J. MANSON AULD, D.Sc. (Lond.), Ph.D. 964

CIX.—Contributions to the Chemistry of the Terpenes. Part V. The Action of Chromyl Chloride on Terpinene and on Limonene. By GEORGE GERALD HENDERSON and WILLIAM CAMERON 969

CX.—Esterification Constants of Substituted Acrylic Acids. Part IV. By JOHN JOSEPH SUDBOROUGH and MORTON JAMES PRICE DAVIES 975

CXI.—The Constitution of the Salts of Barbituric Acid. By JOHN KERFOOT WOOD and EMMA ALEXANDER ANDERSON . 979

CXII.—The Condensation of Amides with Esters of Acetylenic Acids. By SIEGFRIED RUHEMANN 984

CXIII.—Diethoxythioxan; a Relation between the Refractive Power and Chemical Activity of Some Sulphur Compounds. By HANS THACHER CLARKE and SAMUEL SMILES . . . 992

CXIV.—The Influence of Hydroxy- and Alkyloxy-groups on the Velocity of Saponification. Part II. By ALEXANDER FINDLAY and EVELYN MARION HICKMANS, M.Sc. . . . 1004

CXV.—Optically Active Reduced Naphthoic Acids. Part IV. Comparison of the Rotatory Powers of the Di- and Tetrahydronaphthoic Acids with those of Phenylallylacetic, α-Phenylvaleric, β-Phenyl-α-ethyl-, and β-Phenyl-α-methylpropionic Acids. By ROBERT HOWSON PICKARD and JOSEPH YATES 1011

CXVI.—Relation between Chemical Constitution and Physiological Action in the Tropeines. Part II. By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN . . 1020

PAGE

CXVII.—Syntheses with Phenol Derivatives containing a Mobile Nitro-group. Part II. The Interaction of 2:3:5-Trinitro-4-acetylaminophenol and Amines (continued). By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY, A.I.C. 1033

CXVIII.—The Preparation of Disulphides. Part V. Diethyl Esters of α-Dithiodibutyric, α-Dithiodi*iso*butyric, and α-Dithiodi*iso*valeric Acids. By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS 1050

CXIX.—The Chlorination of Acetanilide. By WILLIAM JACOB JONES and KENNEDY JOSEPH PREVITÉ ORTON 1056

CXX.—Acids as Accelerators in Acetylation. Part II. By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITÉ ORTON . 1060

CXXI.—The Action of the Halogens on Aromatic Hydrazines. By FREDERICK DANIEL CHATTAWAY 1065

CXXII.—Some Physical Properties of Radium Emanation. By ROBERT WHYTLAW GRAY and SIR WILLIAM RAMSAY, K.C.B. 1073

CXXIII.—Experiments on the Constitution of the Aloins. Part I. By ROBERT ROBINSON and JOHN LIONEL SIMONSEN . 1085

CXXIV.—The Absorption Spectra of the Nitrates in Relation to the Ionic Theory. By EDWARD CHARLES CYRIL BALY, KATHERINE ALICE BURKE, and EFFIE GWENDOLINE MARSDEN 1096

CXXV.—Studies in Asymmetric Synthesis. Part VIII. The Asymmetric Synthesis of *l*-Mandelic Acid. By ALEX. McKENZIE and HERBERT BROOKE PERREN HUMPHRIES . . 1105

CXXVI.—Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules. Part II. By NORMAN LESLIE GEBHARD and HERBERT BRYAN THOMPSON 1115

CXXVII.—Isolation and Synthesis of *p*-Hydroxyphenylethylamine, an Active Principle of Ergot soluble in water. By GEORGE BARGER 1123

CXXVIII.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XV. Mixed Solvents. By THOMAS STEWART PATTERSON and HARVEY HUGH MONTGOMERIE 1128

CXXIX.—The Action of Phosphorus Pentachloride on Benzamide. By ARTHUR WALSH TITHERLEY and ELIZABETH WORRALL . 1143

CXXX.—The Action of Nitric Acid on the Ethers of Aromatic Hydroxyaldehydes. By ARTHUR HENRY SALWAY . . 1155

CXXXI.—*cyclo*Butane-1:3-dicarboxylic Acid and some of its Derivatives. By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN 1166

CXXXII.—Sodium Sulphite and its Equilibrium with Water. By HAROLD HARTLEY and WILLIAM HENRY BARRETT . 1178

CXXXIII.—The Rate of Formation of Azo-derivatives from Benzenoid Diamines. By VICTOR HERBERT VELEY . . 1186

CXXXIV.—The Molecular Weight of Tetraethylammonium

PAGE

Bromide and the Atomic Weight of Carbon. By ALEXANDER SCOTT 1200

CXXXV.—The Synthesis of Substances allied to Cotarnine. By ARTHUR HENRY SALWAY 1204

CXXXVI.—Monomethyl Lævulose and its Derivatives: Constitution of Lævulosediacetone. By JAMES COLQUHOUN IRVINE and ALEXANDER HYND, M.A., B.Sc. (Berry Scholar in Science) 1220

CXXXVII.—Estimation of Iron by Permanganate in the Presence of Hydrogen Chloride. By JOHN ALBERT NEWTON FRIEND, Ph.D. 1228

CXXXVIII.—The Action of Sulphur Monochloride on Salts of Organic Acids: A Convenient Method of Preparing Anhydrides. By WILLIAM SMITH DENHAM 1235

CXXXIX.—The Velocity of Decomposition of Nitroglycerin by Heat. Part I. By ROBERT ROBERTSON, M.A., D.Sc., F.I.C. 1241

CXL.—The Oxidation of Mucic Acid in Presence of Iron. By FREDERIC FERRABOSCHI 1248

CXLI.—The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides. By EDWARD DE BARRY BARNETT and SAMUEL SMILES 1253

CXLII.—*iso*Quinoline Derivatives. Part I. Oxidation of Laudanosine. By FRANK LEE PYMAN 1266

CXLIII.—The Morphotropic Relationships between the Derivatives of Picric Acid. By GEORGE JERUSALEM . . . 1275

CXLIV.—The Colour and Constitution of Azo-compounds. Part III. By JOHN THEODORE HEWITT and WILLIAM THOMAS . 1292

WOLCOTT GIBBS MEMORIAL LECTURE. By FRANK WIGGLESWORTH CLARKE 1299

CXLV.—Some Derivatives of Anthraquinone. By DOROTHY HARROP, ROLAND VICTOR NORRIS, and CHARLES WEIZMANN . 1312

CXLVI.—The Colour and Constitution of Diazonium Salts. Part I. By GILBERT T. MORGAN and MARY ALCOCK, B.Sc., A.R.C.S 1319

CXLVII.—*iso*Iminazolone. By HENRY JOHN HORSTMAN FENTON and WILLIAM ARTHUR REGINALD WILKS, B.A. . . . 1329

CXLVIII.—Homologues of Furfuraldehyde. By HENRY JOHN HORSTMAN FENTON and FRED ROBINSON, B.A., B.Sc. . . 1334

CXLIX.—Studies of Dynamic Isomerism. Part IX. The Relationship between Absorption Spectra and Isomeric Change. Absorption Spectra of Sulphonic Derivatives of Camphor. By THOMAS MARTIN LOWRY and CECIL HENRY DESCH . 1340

CL.—Studies of the Carbonates. Part I. The Equilibrium between Calcium Carbonate and Carbonic Acid. By CLARENCE ARTHUR SEYLER and PERCY VIVIAN LLOYD . 1347

CLI.—Double and Triple Ferrocyanides of Magnesium, Aluminium, and Cerium with Potassium and Ammonium. By FREDERIC WILLIAM ROBINSON 1353

PAGE

CLII.—The Action of Bromo*cyclo*hexane and of 4-Bromo-1-methyl*cyclo*hexane on the Sodium Derivative of Ethyl Malonate. By Edward Hope and William Henry Perkin, jun. 1360

CLIII.—The Hydrolysis of Amygdalin by Acids. Part I. By J. Wallace Walker and Vernon K. Krieble . . 1369

CLIV.—2:3:5-Trinitro-4-aminophenol and Derivatives. By Raphael Meldola, F.R.S., and James Gordon Hay, A.I.C. 1378

CLV.—The Partial Racemism of Menthyl *r*-Mandelate. By Alexander Findlay and Evelyn Marion Hickmans, M.Sc. 1386

CLVI.—The Colour and Constitution of Azo-Compounds. Part IV. By John Theodore Hewitt and Ferdinand Bernard Thole 1393

CLVII.—The Quantitative Decomposition of the Anilides: a Study in Steric Influence. By Oliver Charles Minty Davis 1397

CLVIII.—Preparation of the Acyl Derivatives of the Aldehyde-cyanohydrins. Part I. By Francis Francis and Oliver Charles Minty Davis 1403

CLIX.—The Carbonates of Copper and the Cupricarbonates. By Spencer Umfreville Pickering, M.A., F.R.S. . . . 1409

CLX.—Constitution of Hydroxyazo-compounds. Part II. Action of Mercuric Acetate on Benzeneazonaphthols. By Alec Duncan Mitchell and Clarence Smith 1430

CLXI.—The Amygdalins. Part I. By J. Wallace Walker and Vernon K. Krieble 1437

CLXII.—The Action of the Grignard Reagent on Phthalic Esters. By Yūji Shibata 1449

CLXIII.—Primary Interaction of Chlorine and Acetanilides. By Kennedy Joseph Previté Orton and William Jacob Jones 1456

CLXIV.—The Conversion of Pinene into Sobrerol. By George Gerald Henderson and Wilfred James Stevenson Eastburn 1465

CLXV.—Influence of Various Sodium Salts on the Solubility of Sparingly Soluble Acids. Part II. By James Charles Philip and Frederick Basil Garner 1466

CLXVI.—Organic Derivatives of Arsenic. Part II. Triaminotriphenylarsine Oxide and Tricamphorylarsinic Acid. By Gilbert T. Morgan and Frances M. G. Micklethwait . 1473

CLXVII.—The Estimation of Arsenic in Organic Compounds. By Harry F. V. Little, Edward Cahen, and Gilbert T. Morgan 1477

CLXVIII.—The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part V. Derivatives of Protocatechuyl Alcohol and Protocatechuonitrile. By Arthur James Ewins 1482

CLXIX.—The Preparation of Disulphides. Part VI. Note on a New Method of Preparing Disulphides. By Thomas Slater Price and Douglas Frank Twiss 1489

PAGE

CLXX.—The Estimation of Carbonates in Presence of Nitrites, Sulphides, or Sulphites by means of Potassium Dichromate. By Ernest Robert Marle 1491

CLXXI.—The Preparation at High Temperatures of some Refractory Metals from their Chlorides. By John Norman Pring and William Fielding 1497

CLXXII.—The Formation and Reactions of Imino-compounds. Part X. The Formation of Imino-Derivatives of Pyrrole and of *iso*Pyrrole from Amino-nitriles. By Stanley Robert Best and Jocelyn Field Thorpe 1506

CLXXIII.—Halogen Derivatives of Cinnamic Acid. By Thomas Campbell James and John Joseph Sudborough . 1538

CLXXIV.—The Constitution of Glucose Derivatives. Part II. Condensation Derivatives of Glucose with Aromatic Amino-compounds. By James Colquhoun Irvine and Robert Gilmour, B.Sc. (Carnegie Scholar) 1545

CLXXV.—The Relation between Viscosity and Chemical Constitution. Part IV. Viscosity and Hydration in Solution. By Albert Ernest Dunstan and Ferdinand Bernard Thole 1556

CLXXVI.—Studies on the Cobaltinitrites. By Mary Cunningham and Frederick Mollwo Perkin 1562

CLXXVII.—The Effect of Contiguous Unsaturated Groups on Optical Activity. Part II. Acids containing Two Adjacent Ethenoid Groups. By Thomas Percy Hilditch (1851 Exhibition Scholar) 1570

CLXXVIII.—The Effect of Contiguous Unsaturated Groups on Optical Activity. Part III. The Normal Series of Fatty Dibasic Acids. By Thomas Percy Hilditch (1851 Exhibition Scholar) 1578

CLXXIX.—Some Derivatives of *l*-Benzoin. By Henry Wren 1583

CLXXX.—Racemisation Phenomena observed in the Study of *l*-Benzoin and its Derivatives. By Henry Wren . . 1593

CLXXXI.—Diketodiphenylpyrroline and its Analogues. By Siegfried Ruhemann 1603

CLXXXII.—*iso*Quinoline Derivatives. Part II. The Constitution of the Reduction Products of Papaverine. By Frank Lee Pyman 1610

CLXXXIII.—The Synthesis of Acridines: Tetramethylacridines, Dimethylnaphthacridines, Naphthaquinacridines, Diquinacridines. By Alfred Senier and Arthur Compton . 1623

CLXXXIV.—The Atomic Weight of Chlorine. By Robert Whytlaw Gray and Frank Playfair Burt . . . 1633

CLXXXV.—The Spontaneous Crystallisation of Solutions of Sodium Carbonate and Sodium Thiosulphate. By Bernard Mouat Jones 1672

CLXXXVI.—The Iodobenzenemonosulphonic Acids. Part I. By Mary Boyle 1683

PAGE

CLXXXVII.—The Influence of Gaseous Oxides of Nitrogen on the Rate of Interaction of Chlorine and Hydrogen. By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON 1717

CLXXXVIII.—Further Syntheses of *p*-Hydroxyphenylethylamine. By GEORGE BARGER and GEORGE STANLEY WALPOLE 1720

CLXXXIX.—The Preparation of Disulphides. Part VII. The Nitrobenzyl Mercaptans and Disulphides. By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS 1725

CXC.—The Benzyl and Nitrobenzyl Selenosulphates and the Benzyl and Nitrobenzyl Diselenides. By THOMAS SLATER PRICE and LIONEL MANFRED JONES 1729

CXCI.—*iso*Quinoline Derivatives. Part III. The Oxidation of Substituted 1-Benzyltetrahydro*iso*quinolines. By FRANK LEE PYMAN 1738

CXCII.—A Method of Harmonising the Atomic Weights. By JAMES MOIR, D.Sc., M.A. 1752

CXCIII.—The Constitution of Polynitrophenols in Alkaline Solution. By BERTRAM HAWARD BUTTLE and JOHN THEODORE HEWITT 1755

CXCIV.—The Solubility of Bismuth Trisulphide in Alkali Sulphides and of Bismuth Trioxide in Alkali Hydroxides. By JOSEPH KNOX (Carnegie Research Fellow of Aberdeen University) 1760

CXCV.—The Volumetric Estimation of Mercury and the Estimation of Silver in Presence of Mercury. By JOSEPH KNOX (Carnegie Research Fellow of Aberdeen University) . . 1768

CXCVI.—A Method for the Measurement of Vapour Pressures. By ALEXANDER CHARLES CUMMING 1772

CXCVII.—Some Mercury Derivatives of Camphor. By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS . 1777

CXCVIII.—Optically Active Substances Containing no Asymmetric Atom. 1-Methyl*cyclo*hexylidene-4-acetic Acid. By WILLIAM HENRY PERKIN, WILLIAM JACKSON POPE, and OTTO WALLACH 1789

CXCIX.—The Action of Ammonia on the Glycide Aryl Ethers. Part I. *o*-Tolyoxypropanolamines. By DAVID RUNCIMAN BOYD and HERBERT STANLEY KNOWLTON 1802

CC.—The Action of Potassium Hydroxide on Epichlorohydrin in Presence of Monohydric Phenols. By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE 1807

CCI.—The Constitution of Hydroxyazo-compounds. Part II. By WILLIAM BRADSHAW TUCK 1809

CCII.—The Iodination of Phenols and the Iodometric Estimation of, and Action of Reducing Agents on, Tannic Acid. By WALTER M. GARDNER, M.Sc., and HERBERT H. HODGSON, M.A., B.Sc., Ph.D. 1819

PAGE

CCIII.—Reactivity of the Halogens in Organic Compounds. Part III. Interaction of Bromoacetic, *a*-Bromopropionic, and *a*-Bromobutyric Acids and their Sodium Salts with Water and with Alkali. By GEORGE SENTER . . . 1827

CCIV.—Ethyl Ether. Part I. The Influence of Water and Alcohol on its Boiling Point. By JOHN WADE, D.Sc., and HORACE FINNEMORE, B.Sc. 1842

CCV.—The Colouring Matters of the Flowers of *Hibiscus sabdariffa* and *Thespasia lampas*. By ARTHUR GEORGE PERKIN 1855

CCVI.—Dynamics of the Reaction between Iodine and Acetone. By HARRY MEDFORTH DAWSON and MAY SYBIL LESLIE, M.Sc. 1860

CCVII.—The Reduction of 4-Hydroxy-*o*-toluic Acid. By OSCAR BAUDISCH, GILBERT STANLEY HIBBERT, and WILLIAM HENRY PERKIN, jun. 1870

CCVIII.—The Reduction of 6-Hydroxy-*o*-toluic Acid. By OSCAR BAUDISCH and WILLIAM HENRY PERKIN, jun . . . 1883

CCIX.—The Reduction of 5-Hydroxy-*m*-toluic Acid. By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and WILLIAM HENRY PERKIN, jun. 1889

CCX.—The Formation and Reactions of Imino-compounds. Part XI. The Formation of 1-Imino-2-cyano*cyclo*pentane from Adiponitrile. By JOCELYN FIELD THORPE . . . 1901

CCXI.—The Action of Mercaptans on Acid Chlorides. Part I. Oxalyl Chloride: the Mono- and Di-thio-oxalates. By HUMPHREY OWEN JONES and HUBERT SANDERSON TASKER . 1904

CCXII.—The Action of Mercaptans on Acid Chlorides. Part II. The Acid Chlorides of Phosphorus, Sulphur, and Nitrogen. By HUBERT SANDERSON TASKER and HUMPHREY OWEN JONES 1910

CCXIII.—Contributions to the Theory of Solutions. By JOHN HOLMES and PHILIP JOHN SAGEMAN 1919

CCXIV.—Studies in Phototropy and Thermotropy. Part I. Arylidene- and Naphthylidene-amines. By ALFRED SENIER and FREDERIC GEORGE SHEPHEARD 1943

CCXV.—The Condensation of Ketone and Aldehydes with the Sodium Derivative of Ethyl Cyanoacetate. Part II. By HENRY DENT GARDNER, jun., and WALTER NORMAN HAWORTH 1955

CCXVI.—The Configuration of Tropine and *ψ*-Tropine, and the Resolution of Atropine. By MARMADUKE BARROWCLIFF and FRANK TUTIN 1966

CCXVII.—Synthesis of Cotarnic Acid. By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and FREDERICK THOMAS . 1977

CCXVIII.—The Constituents of the fruit of *Ecballium Elaterium*. By FREDERICK BELDING POWER and CHARLES WATSON MOORE 1985

CCXIX.—The Resolution of Asymmetrical Derivatives of Phosphoric Acid. By BERNHARD DUNSTAN WILKINSON LUFF (1851 Exhibition Scholar) and FREDERIC STANLEY KIPPING . 1993

PAGE

CCXX.—Synthesis of *cyclo*Hexanone-3-carboxylic Acid. By Mary Elizabeth Dobson, John Ferns, and William Henry Perkin, jun. 2010

CCXXI.—The Acyl-bornylamines. Part I. Fatty Bornylamides. By Percy Faraday Frankland and Fred Barrow 2017

CCXXII.—The Acyl-bornylamines. Part II. Aromatic Bornylamides. By Percy Faraday Frankland and Fred Barrow 2026

CCXXIII.—Ethyl Benzoylacetate. By Edward Hope and William Henry Perkin, jun. 2042

CCXXIV.—Studies in the Camphane Series. Part XXVII. Camphorylphenyltriazen (Camphordiazoaminobenzene) and its Bearing on the Constitution of Diazoamino-compounds. By Martin Onslow Forster and Charles Samuel Garland 2051

CCXXV.—The Triazo-group. Part X. Triazoantipyrine. By Martin Onslow Forster and Robert Müller 2072

Mendeléeff Memorial Lecture. By W. A. Tilden, D.Sc., LL.D., F.R.S., Past-President of the Chemical Society . 2077

CCXXVI.—Syntheses with the Aid of Monochloromethyl Ether. Part II. The Action of Monochloromethyl Ether on the Sodium Derivative of Ethyl Acetoacetate. By John Lionel Simonsen and Robert Storey 2106

CCXXVII.—Syntheses in the Epinephrine Series. By Frank Tutin, Frederic William Caton, and Archie Cecil Osborn Hann 2113

CCXXVIII.—A New Method for the Detection of Sodium, Cæsium, and Rubidium. By Walter Craven Ball . . 2126

CCXXIX.—Direct Proofs of the Presence of the Hydroxyl Group in Derivatives of Anhydroacetonebenzil. By Francis William Gray 2131

CCXXX.—Isomerides of Anhydroacetonebenzil and its Derivatives. By Francis William Gray 2138

CCXXXI.—The Electromotive Behaviour of Cuprous Oxide and Cupric Hydroxide in Alkaline Electrolytes. By Arthur John Allmand 2151

CCXXXII.—A New Synthesis of Oxazole Derivatives. By Robert Robinson 2167

CCXXXIII.—The Correction of the Specific Gravity of Liquids for the Buoyancy of the Air. By John Wade, D.Sc., and Richard William Merriman, B.A. 2174

CCXXXIV.—The Colouring Matter of Cotton Flowers. *Gossypium herbaceum*. Part II. By Arthur George Perkin 2181

CCXXXV.—Synthesis of Hordenine, the Alkaloid from Barley. By George Barger 2193

CCXXXVI.—Volumetric Estimation of Sulphates. By Alec Duncan Mitchell and Clarence Smith 2198

Obituary Notices 2202

Report of the International Committee of Atomic Weights, 1910 2216

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JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*The Affinity Values of Tropine and its Derivatives.*

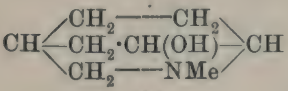
By Victor Herbert Veley.

It seems unnecessary to dwell at any length on the importance of a study of the base tropine, as it forms the starting point of alkaloids in such common use as cocaine, tropacocaine, atropine, homatropine, hyoscyamine, and others. It appears, however, that there are very few data from the physical chemistry standpoint as to the factors of these various substances.

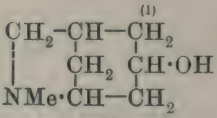
Gaudechon has recently (*Bull. Soc. chim.*, 1907, [iv], 1, 681) determined the heats of combustion, and consequently of formation, of the cocaine and atropine series of alkaloids, and remarked generally that the data obtained by him were in accordance with the accepted views of their constitution. Determinations of the electric conductivity or hydrolysis of the salts are entirely wanting, although it is an interesting point of history that the ancient Peruvians unconsciously practised the latter in that they dried the leaves of the coca plant, mixed them with lime, and used the preparation for chewing, it being their favourite narcotic (compare records of Ondegardo, Acosta, and Herrera). Nearly four hundred years later, the workers of to-day precipitate cocaine from solutions of salts by alkaline solutions, and study the reactions of this base and its congeners when heated under different conditions with the caustic alkalis or alkaline earths.

Various formulæ have been proposed by Ladenburg, Merling, and Willstätter to represent the constitution of tropine, but for the present purpose it is only necessary to discuss briefly those proposed by the two last writers.

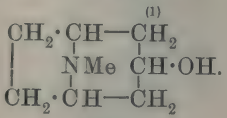
According to Merling (*Ber.*, 1891, **34**, 3108), tropine may be regarded as consisting of conjoint piperidine and hexamethylene residues (formula I) linked in the 1 : 4-positions; Willstätter (*Ber.*, 1897, **30**, 2679) at first represented the base as consisting of conjoint hexamethylene and pyrrolidine residues linked in the 1 : 3-position (formula II), but subsequently (*Ber.*, 1898, **31**, 1534), as consisting of conjoint piperidine and pyrrolidine residues (formula III) linked likewise in the 1 : 3-position:



(I.)



(II.)



(III.)

As regards II and III, it appears to be an open question whether the hydroxyl group is in the 2- or 3-position relatively to that marked (1), but this point is not material to the present inquiry. Ecgonine is derived from tropine by the replacement of hydrogen by the carboxyl group in a position contiguous to that occupied by the hydroxyl, benzoylecgonine is derived from ecgonine by the replacement of the hydroxylic hydrogen atom by the benzoyl group; cocaine is derived from benzoylecgonine by the replacement of the carboxylic hydrogen atom by the methyl group, and, lastly, anhydroecgonine is derived from ecgonine by the abstraction of the elements of water from ecgonine. It appeared possible that some further light might be thrown on the constitution of these several substances by determinations of their affinity values by the methyl-orange or other method, with more especial reference to the presence of (1) a piperidine residue, (2) a pyrrolidine residue, or (3) a piperidine modified by a pyrrolidine, these being the three alternatives with regard to the nitrogen of the several constitutional formulæ proposed for tropine. It has been shown in a previous communication that piperidine and its homologues have a high affinity value, and also that the 1 : 4-derivatives have a higher affinity value than the 1 : 3.

EXPERIMENTAL.

Tropine Hydrochloride.—A crystalline sample of tropine was dissolved in *N*/20-hydrochloric acid so as to form an *N*/20-solution of the hydrochloride; this, as also a solution diluted to half its strength, was examined, with the following results:

$V=4\times10^3$. Temp. 16°.	$V=8\times10^3$. Temp. 18°.	$V=4\times10^3$. Temp. 16°.	$V=8\times10^3$. Temp. 18°.
1·5	0·8	6·2	2·3
3·1	1·6	7·8	2·3
4·6	2·3		

Values of $k=1{\cdot}55$ and $0{\cdot}8$;* hydrolysis values 4·8 and 5·0 respectively; hence $k_{b(16)}=0{\cdot}84\ 10^{-9}$ and $k_{b(18)}=1{\cdot}9\ 10^{-9}$. Although the difference between the two last is rather greater than can be accounted for by variation of temperature, yet both results show that tropine is a weaker base than piperidine, $k_b=1{\cdot}58\ 10^{-3}$, the hydrochloride of which shows no trace of hydrolysis. The difference between the affinity values of tropine and piperidine can be shown by the methyl-orange method in the form of a simple lecture experiment. It would appear, therefore, that formula I should be excluded, and that formula II is the more probable. But as there is an accumulation of independent evidence that tropine and its derivatives, especially ecgonine, can be transformed into pyridine derivatives (Ladenburg, Stöhr, Willstätter, and others), then the only conclusion to be arrived at is that the affinity value of the stronger piperidine residue is modified by being conjoined to the weaker pyrrolidine residue.

Ecgonine Hydrochloride.—A fine crystalline sample (Merck) was dissolved in water, and the solution diluted as in other cases of considerable hydrolysis. The following results were obtained at 14°:

$V=8\times10^4$.	$V=4\times10^4$.	$V=8\times10^4$.	$V=4\times10^4$.
1·5	2·9	7·1	14·5
2·8	5·8	8·5	14·5
4·2	8·7	9·8	14·5
5·6	11·6	11·3	14·5

Values of $k=1{\cdot}4$ and $2{\cdot}9$, corrected 1·42 and 2·85 respectively; hydrolysis value = 89·7. This last, as intermediate between that found for sarcosine, 87·5, and betaine, 94·7 (Trans., 1908, **93**, 662; compare Winkelblech, *Zeitsch. physikal. Chem.*, 1901, **36**, 574), shows that ecgonine is of the order of an amphoteric electrolyte, and Willstätter's view, that it is probably an inner anhydride or betaine (*loc. cit.*, p. 1540), is confirmed.

Anhydroecgonine Hydrochloride.—This substance was dealt with precisely as the above, and the following results were obtained at 14°:

$V=8\times10^4$.	$V=4\times10^4$.	$V=8\times10^4$.	$V=4\times10^4$.
1·1	2·1	5·4	8·4
2·1	4·2	6·4	8·4
3·1	6·3	7·4	8·4
4·3	8·4	8·5	8·4

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* The factors for hydrochloric acid are those given in my previous communication (Trans., 1908, **93**, 656).

Values of $k = 1{\cdot}05$ and $2{\cdot}1$ respectively; hydrolysis value $= 65{\cdot}6$, $k_{b(14)} = 3{\cdot}68\ 10^{-11}$; this last figure is almost identical with that, $3{\cdot}4\ 10^{-11}$, found by Cumming for 1:3-benzobetaine (*Proc. Roy. Soc.*, 1906, **78**, *A*, 136). Anhydroecgonine is thus more basic or less acid than ecgonine but it is not possible in the present state of knowledge to attribute this result to the presence of a tetrahydro- in the stead of a hexahydropyridine residue.

Benzoylecgonine Hydrochloride.—Benzoylecgonine was dissolved in such a volume of *N*/20-hydrochloric acid so as to form an *N*/20-solution, presuming that no hydrolysis occurred. The solution was diluted and dealt with as in the preceding cases, but the factor found was identical with that of hydrochloric acid of the same concentration, or, in other words, the solution behaved as if the benzoylecgonine was not present; thus showing that under the conditions of experiment no combination between the two substances had taken place. It is generally stated that benzoylecgonine possesses both a basic and an acidic function, but the former must be of the order of caffeine, the hydrochloride of which was found to give a hydrolysis value of 97·2 under precisely similar conditions of experiment (Trans., 1908, **93**, 664).

Cocaine Hydrochloride.—An *N*/20 and more dilute solutions of this salt showed no hydrolysis with methyl-orange, but as the alkaloid is displaced from solutions of its salts by ammonia solution, its affinity value would lie between the limits $1\ 10^{-5}$ and $1\ 10^{-7}$. The *N*/20-solution was heated to boiling in a Jena glass flask fitted with an inverted condenser for four hours, and the acidity found after this treatment was equal to one per cent. in terms of hydrochloric acid.

It was not possible, however, to prove directly whether this result was due (1) to the hydrolysis of the hydrochloride, (2) to a partial resolution of cocaine into benzoylecgonine and methyl alcohol, or (3) a conjoint effect of (1) and (2). It has been shown by Einhorn (*Ber.*, 1888, **21**, 48) that cocaine when boiled with water is resolved into benzoylecgonine and methyl alcohol, although this change requires a long time for its completion, and also by Breteau (*J. Pharm. Chim.*, 1906, [vi], **23**, 474) that a sample of cocaine hydrochloride, originally damp, was found after a lapse of years to contain methyl benzoate, benzoic acid, and ecgonine hydrochloride.

The decomposition of cocaine, as also of its isomeride, α-cocaine, under varied conditions, might form a subject of an investigation of considerable practical importance, but however this may be, it is evident that cocaine, or the methyl ester of benzoylecgonine, is a very much stronger base than its corresponding acid, benzoylecgonine. This result is in complete accordance with those obtained by Johnson (*Proc. Roy. Soc.*, 1906, **78**, *A*, 96) for methylglycine, and myself for ethylglycine (*loc. cit.*, 662), as compared with those of glycine, both of which concur in showing that the substitution of the carboxylic hydrogen atom by hydrocarbon groups in the case of an amino-acid destroys the amphoteric electrolytic character of such an acid. The difference between the composition of solutions of benzoylecgonine and cocaine hydrochlorides can readily be shown by the methyl-orange method as a simple lecture experiment.

An attempt was made to determine approximately the affinity value of cocaine by an independent method, possibly of general applicability for other alkaloids which are relatively strong bases. The method is based on the determination of the mass of sodium hydroxide required to produce an initial precipitation of the alkaloid from an aqueous solution of a given mass of its hydrochloride; the method can only be applied in cases in which the alkaloid is sufficiently insoluble, and its hydrochloride sufficiently soluble, in water. But as no process has as yet been devised for determining with any degree of accuracy the strength of a sodium hydroxide solution of titre value $N/1000$ or thereabouts, solutions of sodium salts known to be partly hydrolysed into the free acid and base were substituted. After preliminary trials, borax was selected as possessing the two practical advantages, (1) that it is readily procurable in a great degree of purity, and (2) that it and the alkaloid hydrochlorides are in common use in surgical operations. If it is assumed that the unaltered salt and the liberated acid produce no appreciable effect on the course of the reaction, then Guldberg and Waage's equilibrium formula may be applied, thus:

Before initial precipitation we have:

$$\text{Cocaine hydrochloride} + \text{sodium hydroxide} \rightleftarrows \text{sodium chloride} + \text{cocaine};$$

and if M_1, M_2, M_3, and M_4 be the respective masses of the four substances in solution, then

$$M_1M_2/M_3M_4 = k_1/k \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

in which k_1 and k are the relative affinities of sodium hydroxide and cocaine for hydrochloric acid. But as the chlorine ion is common to both sides of the chemical equation, then we have simply

$$M_2/M_4 = k_1/k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

or the relative masses of the two bases will give their relative affinities for hydrochloric acid up to the point at which a state of homogeneous equilibrium, all four substances remaining in solution, passes into a state of heterogeneous equilibrium, namely, the precipitation of the alkaloid.

It was found that 0·5 c.c. of an $N/10$-solution of borax (anhydrons) sufficed to produce an initial precipitation of cocaine from 10 c.c. of an

$N/20$-solution of the hydrochloride, and also that 0·26 c.c. of the same borax solution produced a like result with the same volume of an $N/40$-solution of the salt, the precipitation in the latter case taking a rather longer time to become apparent. Taking the former result, there are the following data: 1 c.c. $N/10$-borax solution contains 20·2 milligrams of salt, but such a solution is hydrolysed to the extent of 1 per cent.* (actual figure, 0·95 per cent.); hence the hydrolysed portion is equivalent to 0·202 milligram, and the amount of sodium hydroxide corresponding therewith is 0·08 milligram. But 10 c.c. of an $N/20$-solution of cocaine hydrochloride contain 151·6 milligrams of alkaloid, and 0·04 milligram of sodium hydroxide sufficed to upset the equilibrium of the amount of alkaloid in combination with hydrochloric acid. Hence ratio of affinity of sodium hydroxide and cocaine relative to hydrochloric acid $= 151\cdot6 : 0\cdot04 = 3790 : 1$; but, according to Ostwald, the ratio of affinity of sodium hydroxide to ammonia $= 100 : 1\cdot8$; hence ratio of affinity of ammonia to cocaine $= 3790/1000 \times 1\cdot8 = 68\cdot2$. The affinity value of ammonia is $k_{(b)} = 1\cdot7\ 10^{-5}$; hence that of cocaine $= 1\cdot7\ 10^{-5}/68 = 2\cdot5\ 10^{-7}$.

The limit value of the methyl-orange method is somewhat less than $1\ 10^{-7}$; cocaine hydrochloride should, if the above data are correct, show no hydrolysis at the ordinary temperature with methyl-orange, but the solution, when heated, would in all probability show traces of hydrolysis. Such a conclusion is in perfect agreement with the observations recorded above.

The method proposed implies the assumptions: (1) that, as stated above, the effects produced by substances in solution other than the sodium hydroxide and alkaloid hydrochloride are inconsequent; and (2) that the ratio value of affinities of soda and ammonia, and the value of k_a given for boric acid, are substantially correct.

It is proposed to give at an early date some further determinations of the affinity values obtained by the above method, but, meanwhile, subject to such revisions given above, the plea may reasonably be put forward that it is better to have approximate values for the affinity numbers of the alkaloids in daily use as drugs rather than to have none at all, which up to the present time has been the state of affairs.

Tropeines.—The hydrochlorides of two substances of this type were examined, namely, atropine, the tropeine of tropic acid, and homatropine, the tropeine of mandelic acid, but neither showed any appreciable hydrolysis even after their solutions had been heated to the boiling point for four hours. It would thus appear (1) that their affinity values are higher than $1\ 10^{-7}$, and (2) that no conversion of the lactonic group into the corresponding hydroxy-acid, thus:

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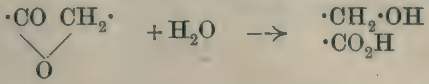
* Shields (*Zeitsch. physikal. Chem.*, 1893, **12**, 187) gives the hydrolysis value of an $N/10$-borax solution $= 0\cdot5$ per cent.; although the figure has found its way into text-books, yet it was arrived at by results very far from concordant, as this author himself admitted. The number given above has been calculated from Lundén's recent value for boric acid, $k_{a(15)} = 5\cdot48\ 10^{16}$, by means of the approximate equation $x = \sqrt{Vk_w/k_a}$.



took place, such a change being the probable explanation of the difference in physiological activity, namely, mydriasis, between aqueous and alkaline solutions of such tropeines (compare Jowett and Marshall, Trans., 1900, **77**, 481; Jowett and Hann, *ibid.*, 1906, **89**, 357).

Hyoscyamine was also examined, and its behaviour was similar to those of atropine and homatropine.

Summary.

(1) It is shown that tropine, the parent base of the atropine and cocaine alkaloids, has a lower affinity value than piperidine, and it is concluded that the stronger piperidine residue is modified by being conjoined to the weaker pyrrolidine residue if the constitution most recently proposed by Willstätter is taken as substantially correct.

(2) Ecgonine, the carboxylic acid of tropine, possesses all the properties of an amphoteric electrolyte, and Willstätter's view, that it is of the nature of an inner anhydride or betaine, is confirmed.

(3) Anhydroecgonine is a stronger base than ecgonine; the value obtained is approximately equal to that of a betaine of the aromatic series.

(4) Benzoylecgonine in dilute solution does not remain in combination with hydrochloric acid, and its basic function is of the order of caffeine.

(5) Cocaine is a relatively strong base, although weaker than ammonia; the effect produced by the substitution of the carboxylic hydrogen in benzoylecgonine by the methyl group is quite analogous to that previously observed in the case of glycine. The affinity value of cocaine was found to be approximately $k_b = 2{\cdot}5\ 10^{-7}$ by determining the mass of sodium hydroxide contained in a hydrolysed borax solution which was required to upset the equilibrium between a certain mass of cocaine combined with hydrochloric acid.

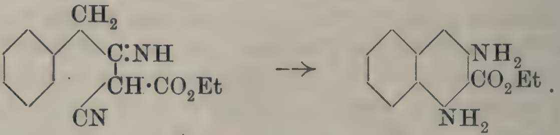
(6) The tropeines, atropine, and homatropine have an affinity value greater than $k_b = 1\ 10^{-7}$, and $N/20$-solutions of their hydrochlorides show no appreciable hydrolysis when heated to the boiling point.

In conclusion, I have to express my obligations to the Research Fund Committee of the Chemical Society, for a grant for purchase of materials, and also to Messrs. Burroughs, Wellcome & Co., for kindly presenting me with certain samples of alkaloids and their salts for the purpose of this investigation.

II.—*The Formation and Reactions of Imino-compounds. Part VII. The Formation of* 1:3-*Naphthylenediamine from β-Imino-α-cyano-γ-phenylpropane.*

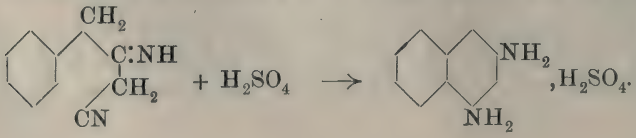
By Stanley Robert Best and Jocelyn Field Thorpe.

In a former part of this series (Trans., 1906, **89**, 1906), attention was drawn to the formation of ethyl 1:3-naphthylenediamine-2-carboxylate by the action of cold concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-phenylbutyrate, thus:



It was, moreover, shown in later parts of the series (Trans., 1907, **91**, 578, 1004, 1687) that the formation of the naphthalene ring could also be effected from a number of similar imino-nitriles by the aid of the same reagent. In all the compounds investigated, however, a carbethoxyl group was attached to the carbon atom united with the nitrile group; and in order to show that the formation of the naphthalene ring in this manner is of general application, it was necessary to investigate the behaviour of a benzenoid imino-nitrile constituted as above, but containing the group $-CH_2·CN$. In this way any influence which might be exerted by the mobile hydrogen atom present, when, for example, a carbethoxyl group is attached to this carbon atom, would be eliminated.

A compound of this class is β-imino-α-cyano-γ-phenylpropane, which, if a second substituting group attached to the α-carbon atom is without effect, would be converted by the aid of concentrated sulphuric acid into the sulphate of 1:3-naphthylenediamine, thus:



Many unexpected difficulties were, however, met with in attempting to synthesise this imino-nitrile. Holzwart has shown (*J. pr. Chem.*, 1889, [ii], **39**, 242) that β-imino-α-cyano-β-phenylethane,

$$NH{:}CPh{\cdot}CH_2{\cdot}CN,$$

can be readily prepared by the action of sodium on an equimolecular mixture of acetonitrile and benzonitrile in dry ethereal solution, and our own experiments have also shown that the same product can be produced by the action of a trace of sodium ethoxide on a mixture of the two nitriles dissolved in alcohol; but on applying either of these reactions to a mixture of phenylacetonitrile and acetonitrile, the sole product was found to be β-imino-α-cyano-αγ-diphenylpropane,

$$CH_2Ph{\cdot}C({:}NH){\cdot}CHPh{\cdot}CN,$$

which had evidently been formed by the condensation of phenylacetonitrile with itself.

Ultimately the desired result was obtained by the hydrolysis of ethyl β-imino-α-cyano-γ-phenylbutyrate,

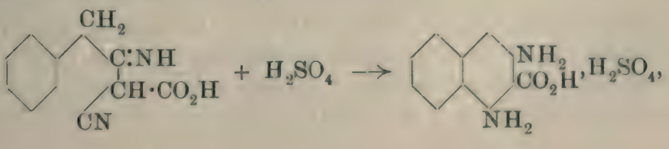
$$CH_2Ph{\cdot}C({:}NH){\cdot}CH(CN){\cdot}CO_2Et,$$

a method for the preparation of which in quantity has already been given (Trans., 1906, **89**, 1916). This ethyl salt is, however, remarkably stable towards alkaline hydrolysing agents; thus, when the ethyl salt is boiled with one equivalent of potassium hydroxide dissolved in methyl alcohol, it is completely converted into methyl β-imino-α-cyano-γ-phenylbutyrate, $CH_2Ph{\cdot}C({:}NH){\cdot}CH(CN){\cdot}CO_2Me$, and if water is present, hydrolysis takes place at the imino-group with the formation of the potassium salt,

$$CH_2Ph{\cdot}C(OK){:}C(CN){\cdot}CO_2Me,$$

which yields, on acidifying, methyl α-cyano-γ-phenylacetoacetate, $CH_2Ph{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Me$, identical with the compound prepared by Haller and Blanc (*Compt. rend.*, 1900, **130**, 1594) by the action of phenylacetyl chloride on the sodium compound of methyl cyanoacetate. No trace of the carboxylic acid could be isolated in this way, but it was subsequently found that if the methyl or ethyl salt is heated with alcoholic sodium ethoxide, it is slowly converted into the sodium salt of the acid, $CH_2Ph{\cdot}C({:}NH){\cdot}CH(CN){\cdot}CO_2Na$, from which the free carboxylic acid can be readily prepared on acidifying.

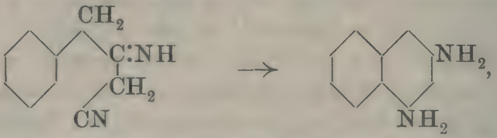
β-Imino-α-cyano-γ-phenylbutyric acid, when treated with ice-cold concentrated sulphuric acid, passes at once into the sulphate of 1 : 3-naphthylenediamine-2-carboxylic acid,



and, since this salt is readily dissociated by water, the free carboxylic acid is obtained on pouring the strongly acid solution on ice.

β-Imino-α-cyano-γ-phenylbutyric acid readily loses carbon dioxide on being heated at 140°, and β-imino-α-cyano-γ-phenylpropane can be isolated from the product in a crystalline condition.

This substance, on treatment with cold concentrated sulphuric acid passes at once into the sulphate of 1:3-naphthylenediamine,



and it is therefore evident that it is immaterial whether one of the hydrogen atoms attached to the α-carbon atom of an imino-nitrile of this type is substituted or not in order that the nitrile may be converted into a naphthalene derivative by the aid of concentrated sulphuric acid. It is, of course, essential that one of these hydrogen atoms should remain unsubstituted.

EXPERIMENTAL.

Methyl β-Imino-α-cyano-γ-phenylbutyrate, $CH_2Ph\cdot C(:NH)\cdot CH(CN)\cdot CO_2Me$.

This methyl salt was prepared in an attempt to hydrolyse ethyl β-imino-α-cyano-γ-phenylbutyrate to the corresponding carboxylic acid by the aid of the theoretical quantity of potassium hydroxide dissolved in absolute methyl alcohol. The theoretical quantity of the alkali was used in this experiment, because it has already been shown (Trans., 1906, **89**, 1919) that excess of this reagent readily decomposes this ethyl salt into malonic and phenylacetic acids, and, therefore, considerable care had to be exercised in order to prevent the disruption of the chain. Ten grams of ethyl β-imino-α-cyano-γ-phenylbutyrate were added to a solution containing 2·4 grams of pure potassium hydroxide dissolved in methyl alcohol, and the solution was boiled for one hour. Water was then added, and the solid which separated was collected and crystallised from dilute methyl alcohol. The methyl salt forms slender, colourless needles melting at 98°:

0·1573 gave 0·3840 CO_2 and 0·0807 H_2O. C = 66·58; H = 5·7.

$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

The transformation of the ethyl into the methyl salt in this experiment is, excepting for the small quantity of the corresponding ketone isolated in the manner described below, almost quantitative. No trace of unaltered ethyl salt could be detected in the mother liquors from the crystallisation of the methyl salt.

Methyl α-Cyano-γ-phenylacetoacetate, $CH_2Ph\cdot CO\cdot CH(CN)\cdot CO_2Me$.

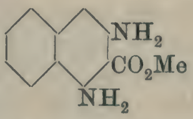
The alkaline solution, after separating the imino-nitrile in the above experiment, on being acidified with hydrochloric acid yielded an oil, which rapidly became solid on scratching. It was collected and recrystallised from dilute methyl alcohol, yielding long, slender needles melting at 53°. The ester dissolves in sodium hydrogen carbonate solution with effervescence:

0·1612 gave 0·3912 CO_2 and 0·0754 H_2O. C = 66·18; H = 5·19.

$C_{12}H_{11}O_3N$ requires C = 66·3; H = 5·1 per cent.

This substance is therefore evidently methyl α-cyano-γ-phenylacetoacetate, although the melting point is 8° lower than that given by Haller and Blanc (*loc. cit.*). Although we have subjected the compound prepared by us to repeated recrystallisation, we have been unable to isolate a compound melting higher than 53°. The formation of this ketone is quantitative if water is present during the above hydrolysis.

Methyl 1 : 3-*Naphthylenediamine-2-carboxylate*,



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This methyl salt was prepared by the action of cold concentrated sulphuric acid on methyl β-imino-α-cyano-γ-phenylbutyrate. Ten grams of the salt were slowly added in a finely-ground condition to 50 grams of concentrated sulphuric acid, the acid being kept cool throughout the operation by means of running water. When all had been added, the deep green sulphuric acid solution, after being kept at the ordinary temperature for fifteen minutes, was poured on ice, and the solution filtered to remove a small quantity of precipitated matter. The oil which was precipitated from this solution by the addition of excess of ammonia was then extracted with ether, and the deep yellow ethereal solution shaken with dilute hydrochloric acid until colourless. The free base was precipitated on rendering the hydrochloric acid washings alkaline, and was purified by recrystallisation from methyl alcohol. *Methyl* 1 : 3-*naphthylenediamine*-2-*carboxylate* forms small, bright yellow plates melting at 119°:

0·2005 gave 0·4891 CO_2 and 0·0980 H_2O. C = 66·54; H = 5·43.

$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

Like the corresponding ethyl salt, methyl 1 : 3-naphthylenediamine-2-carboxylate dissolves in dilute mineral acids, forming colourless solutions. The *hydrochloride* is precipitated in white needles from a solution of the base in dilute hydrochloric acid on the addition of excess of concentrated acid:

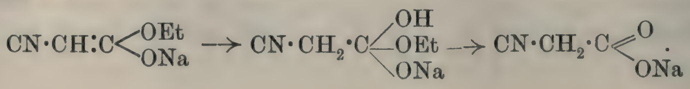
0·2113 gave 0·2093 AgCl. Cl = 24·52.

$C_{12}H_{12}O_2N_2,2HCl$ requires Cl = 24·56 per cent.

When ethyl 1 : 3-naphthylenediamine-2-carboxylate is warmed with a methyl-alcoholic solution of the equivalent quantity of potassium hydroxide, the crystalline potassium salt of 1 : 3-naphthylenediamine-2-carboxylic acid slowly separates (compare Trans., 1906, **89**, 1921), which yields the corresponding acid, melting at 85°, on acidifying its aqueous solution. When the free carboxylic acid is heated at 100°, carbon dioxide is evolved and 1 : 3-naphthylenediamine, melting at 96°, is produced.

β-Imino-α-cyano-γ-phenylbutyric Acid, $CH_2Ph{\cdot}C(\colon NH){\cdot}CH(CN){\cdot}CO_2H$.

The partial hydrolysis of ethyl β-imino-α-cyano-γ-phenylbutyrate was ultimately effected by the aid of an alcoholic solution of sodium ethoxide, and it is probable that the mechanism of this hydrolysis is as follows: It has already been shown that ethyl β-imino-α-cyano-γ-phenylbutyrate reacts only partly with cold alcoholic sodium ethoxide, and that if the product is treated with methyl iodide, only a small proportion of the ethyl salt is converted into ethyl β-imino-α-cyano-γ-phenylvalerate, $CHMePh{\cdot}C(\colon NH){\cdot}CH(CN){\cdot}CO_2Et$ (compare Trans., 1906, **98**, 1922). From this experiment, it would appear as if the hydrogen atom of the cyanoacetic residue in ethyl β-imino-α-cyano-γ-phenylbutyrate is not replaceable by sodium—at any rate, by the action of cold sodium ethoxide. It is, however, probable that, on prolonged treatment with excess of sodium ethoxide at a higher temperature, a partial replacement of this hydrogen atom does ensue, and that there is formed a disodium derivative of the formula $CHPhNa{\cdot}C(\colon NH){\cdot}CNa(CN){\cdot}CO_2Et$. When this compound is acted on by water, the sodium atom attached to the benzyl residue is replaced in the ordinary manner by hydrogen, but the sodium combined with the cyanoacetic residue reacts in the same way as the sodium derivative of ethyl cyanoacetate, and gives the sodium salt of the corresponding acid. For the sake of clearness, it may be well to recall the behaviour of the sodium compound of ethyl cyanoacetate towards water, which has been previously recorded (Trans., 1900, **77**, 925), and the explanation which was then given; for it was shown that when ethyl sodiocyanoacetate is treated with ice-cold water, no trace of ethyl cyanoacetate is recovered, and the solution contains only the sodium salt of cyanoacetic acid. The explanation then suggested was in accordance witn the following scheme:



$$\mathrm{CN{\cdot}CH{:}C}\Big\langle{}^{\mathrm{OEt}}_{\mathrm{ONa}} \longrightarrow \mathrm{CN{\cdot}CH_2{\cdot}C}\begin{matrix}\diagup\mathrm{OH}\\ -\mathrm{OEt}\\ \diagdown\mathrm{ONa}\end{matrix} \longrightarrow \mathrm{CN{\cdot}CH_2{\cdot}C}\Big\langle{}^{\mathrm{O}}_{\mathrm{ONa}}\ .$$

It is true that we have no direct evidence of the formation of the disodium salt of ethyl β-imino-α-cyano-γ-phenylbutyrate to which reference has been made above, since an experiment made with the object of forming a dimethyl derivative by the action of methyl iodide yielded only the monomethyl derivative; but in view of the remarkable stability of ethyl β-imino-α-cyano-γ-phenylbutyrate towards alcoholic potash, this explanation seems to possess a greater degree of probability than that which involves the direct hydrolysis of the ethyl salt to the sodium salt of the acid, with the consequent formation of diethyl ether.

In order to prepare the acid, the following conditions were found to yield the best results: Twenty grams of the ethyl salt were mixed with an alcoholic solution of 4 grams of sodium, and the clear solution, which must contain sufficient alcohol to prevent the iminonitrile from separating on cooling, transferred to a Carius tube, which, after being sealed, was heated at 100° for three hours. The product was then poured into water, and the oily mass which separated extracted with ether. The ethereal solution was then washed with dilute sodium carbonate solution, and the alkaline washings, after being freed from ether on the water-bath, were acidified by means of hydrochloric acid. The oil which then separated rapidly solidified, and, after being collected, was recrystallised from alcohol. *β-Imino-α-cyano-γ-phenylbutyric acid* forms colourless prisms melting and decomposing at 138°:

0·1513 gave 0·3617 CO_2 and 0·0681 H_2O. C = 65·20; H = 5·01.

$C_{11}H_{10}O_2N_2$ requires C = 65·3; H = 4·9 per cent.

The acid is soluble in hot water, and can be recrystallised from this solvent, but some loss is entailed in the process, owing to the decomposition of the acid into carbon dioxide and β-imino-α-cyano-γ-phenylpropane. The constitution of the acid was proved by its conversion into phenylacetic and malonic acids by the action of excess of aqueous potassium hydroxide. The *silver* salt separates from a neutral solution of the ammonium salt on addition of the theoretical quantity of silver nitrate solution as a white, microcrystalline precipitate:

0·2216 gave 0·0772 Ag. Ag = 34·84.

$C_{11}H_9O_2N_2Ag$ requires Ag = 34·87 per cent.

The ethereal solution, from which the above acid had been extracted, yielded an oil on evaporation, from which a quantity of unchanged ethyl β-imino-α-cyano-γ-phenylbutyrate separated on standing. The yield of the acid by this process is only about 30 per cent., but the crude ethyl salt recovered from the experiment can be used again without further purification, and thus a considerable quantity of the acid can be readily obtained.

Conversion of β-Imino-α-cyano-γ-phenylbutyric Acid into 1 : 3-Naphthylenediamine-2-carboxylic Acid.

This conversion is readily effected by the aid of concentrated sulphuric acid in the following way: Five grams of the acid are added slowly to 15 grams of concentrated sulphuric acid cooled in ice, and, when all has dissolved, the deep green solution, after being kept at the ordinary temperature for fifteen minutes, is poured on ice. The acid separates at once as a white precipitate, which, after crystallisation from warm water, is obtained in colourless needles melting at 85°:

0·1808 gave 0·4320 CO_2 and 0·0852 H_2O. $C=65·17$; $H=5·21$.

$C_{11}H_{10}O_2N_2$ requires $C=65·3$; $H=4·9$ per cent.

The acid was proved to be 1 : 3-naphthylenediamine-2-carboxylic acid by the fact that on boiling with water it was slowly converted into 1 : 3-naphthylenediamine melting at 96°.

β-Imino-α-cyano-γ-phenylpropane, $CH_2Ph·C(:NH)·CH_2·CN$.

This imino-nitrile was prepared by heating β-imino-α-cyano-γ-phenylbutyric acid above its melting point until the evolution of carbon dioxide had ceased, and was isolated in the following manner: Five grams of the acid were placed in a test-tube, and heated in a bath of sulphuric acid at 140° until the evolution of carbon dioxide had finished, an operation which required about fifteen minutes. The liquid was then cooled, mixed with a little alcohol, and the alcoholic solution filtered. After being decolorised with animal charcoal, a little water was added, and, after some time, crystals separated slowly from the clear solution. These were collected and recrystallised from alcohol, yielding colourless needles melting at 48°:

0·1723 gave 0·4794 CO_2 and 0·0994 H_2O. $C=75·88$; $H=6·41$.

$C_{10}H_{10}N_2$ requires $C=76·0$; $H=6·3$ per cent.

The imino-nitrile is readily hydrolysed by excess of aqueous potassium hydroxide, yielding phenylacetic and malonic acids.

Conversion of β-Imino-α-cyano-γ-phenylpropane into 1 : 3-*Naphthylenediamine.*

When 3 grams of the imino-nitrile are slowly added to 9 grams of well-cooled concentrated sulphuric acid, a pale green solution is produced, and, after the lapse of fifteen minutes, a clear solution is obtained on pouring the mixture into water. On rendering the solution alkaline with ammonia, a crystalline precipitate separates on standing, which, on being collected and recrystallised from hot water, yields small plates melting at 96°:

0·1687 gave 0·4697 CO_2 and 0·0972 H_2O. C = 75·93; H = 6·4.

$C_{10}H_{10}N_2$ requires C = 76·0; H = 6·3 per cent.

The compound is evidently therefore 1 : 3-naphthylenediamine.

Part of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

MANCHESTER UNIVERSITY.

III.—*The Optical and Sensitising Properties of the* iso*Cyanine Dyes.*[*]

By SAMUEL EDWARD SHEPPARD (1851 Exhibition Scholar).

THE *iso*cyanines are a class of dyes analogous to the cyanines, but derived from quinaldine; their structural formula has not yet been clearly established, but it appears that we may assume the presence of a quinaldine and a quinoline nucleus. In the course of an investigation of their properties as photographic sensitisers, certain results of general photochemical interest were obtained, a short account of which is here given.

Absorption of Light by iso*Cyanine Solutions.*

The measurements were made in an improved form of the Hüfner spectrophotometer.[†] As a measure of the absorption, the Bunsen extinction-coefficient was taken: $E = 1/d \log \frac{I}{I_o}$, where d is the thickness traversed, I_o the original intensity of light, and I that after absorption. From this, the Vierordt absorption ratio $A = C/\epsilon$ is obtained, C being the concentration; as units, 1 cm. and grams per litre were employed. If Beer's law holds, the ratio C/ϵ should remain constant. Aqueous *iso*cyanine solutions are very sensitive towards acid, even the atmospheric carbon dioxide bleaching them, so that the measurements were made in alcohol. The absorption-curves show two maxima; that near the red is termed the α-band, the other, the β-band. For the dye used, the maxima lay at 540 μμ and 575 μμ in alcohol, at 545 μμ and 580 μμ in chloroform, at which points the measurements were made. The results of three series in alcohol are tabulated.

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[*] Fuller details as to the technical and photochemical results will be found in the *Photographic Journal* (Transactions of the Royal Photographic Society).

[†] The apparatus, etc., is described in the *Theory of the Photographic Process*, by S. E. Sheppard and C. E. K. Mees (Longmans).

TABLE I.

Concentration.	A at 540 μμ.	A at 575 μμ.
0·200	0·001083	—
0·100	0·001149	0·00605
0·050	0·001135	0·00586
0·025	0·001219	0·00615
0·020	0·001115	—
0·0125	0·001309	0·00678
0·0100	0·001144	0·00605
0·0050	0·001175	0·00608
0·0025	0·001239	0·00625
0·00125	0·001395	0·00640

In spite of some discrepancy, it appears that Beer's law is followed in alcohol and this occurs, although conductivity measurements indicate a progressive dissociation. The increase of A in the lowest numbers, whilst in the opposite sense to that required by the application of the ionic theory, is probably due to the aforementioned influence of carbon dioxide. More consistent results were obtained in chloroform.

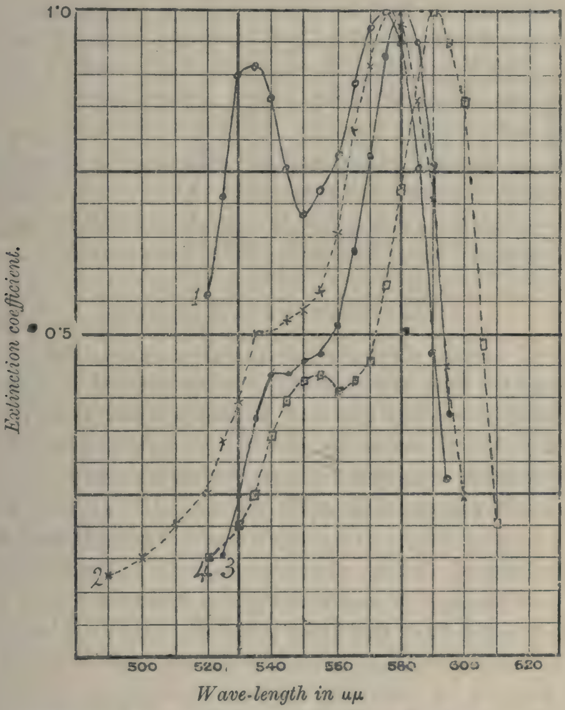
TABLE II.

Concentration.	ϵ at 545 μμ.	A.
0·1200	1·797	0·001112
0·0100	0·910	0·001101
0·0050	0·454	0·001105
0·0025	0·227	0·001100
0·00125	0·106	0·001170

Although carbon dioxide is more soluble in chloroform, the concentration of the hydrogen ion which produces the bleaching is lower. As Beer's law is followed in alcohol while dissociation is in progress, and as solutions in comparatively non-dissociating solvents show the same absorption and intensity of colour as those in alcohol and water, it is concluded that *the absorption of light by solutions of the* isocyanine *dyes is independent of ionisation.* On the assumption of a causal connexion between structure and colour, it always appeared difficult to conceive that undissociated molecule and ion should possess the same chromophore, and yet one be colourless, the other coloured. The position of Hantzsch (*Ber.*, 1900, **33**, 278) appears more logical; a change from a colourless to a coloured condition always implies an alteration in structure. Green and King (Trans., 1906, **89**, 518) have shown the inadequacy of the unmitigated ionic theory as applied to phenolphthalein.

Influence of Solvent.

It is well known that the absorption spectrum of a dye depends in many cases on the solvent. Kundt formulated the rule that the absorption is displaced toward the red as the dispersion of the solvent increases, but many exceptions have been found. Measurements with an *iso*cyanine were made in the following solvents: water (aqueous alkali), alcohol, 25 per cent. alcohol, acetone, toluene, chloroform, quinoline. The results obtained from the absorption-curves were as follows:



1. *Curve for water.*
2. *Curve for alcohol.*
3. *Curve for toluene.*
4. *Curve for quinoline.*

Solvent..........	Water.	Acetone.	Alcohol.	Toluene.	Chloroform.	Quinoline.
Maximum	575 $\mu\mu$	577 $\mu\mu$	577 $\mu\mu$	580 $\mu\mu$	583 $\mu\mu$	590 $\mu\mu$

The progressive displacement of the absorption is shown in the accompanying curve.

The result was the same whether the solutions were prepared directly or by the addition of concentrated alcoholic solution to the other solvents. It will be seen that Kundt's law holds. The author is of the opinion that this is an expression of a state of association between the solvent and solute, a "weighting" of the molecule thus taking place. The question is more fully discussed in another place, as well as its relation to the theory of sensitising. Possibly the action of the solvent is of a similar nature to that exercised on the optical rotatory power of dissolved substances.

Relation of Absorption to Constitution.

The absorption curves of some thirteen *iso*cyanines have been measured; the details are chiefly of technical interest, and are given elsewhere. Briefly, it may be stated that increase in the molecular weight by the substitution of heavy groups shifts the absorption toward the red (Nietzki's rule). Further substitution in either the quinaldine or the quinoline nucleus affects both absorption bands simultaneously, although not necessarily to the same extent. On the whole, substitution in the quinaldine nucleus appears most effective, the alkyloxy-group being the most efficient auxochrome.

The iso*Cyanines as Sensitisers.*

Whilst, of course, chiefly of technical moment, the sensitising of silver halides by dyes possesses also a more general interest. Theory of any kind must explain two sets of phenomena: firstly, the process by which the dye is taken up and retained by the halide: secondly, the photochemical reaction in virtue of which the halide becomes developable on exposure to such wave-lengths as are absorbed by the dye. As regards the first, which may be regarded as part of the general problem of dyeing, experiments with the *iso*cyanines support the view that the dye forms an absorption compound with the halide; thus it was found that the most prolonged washing leaves a definite proportion of dye associated with the halide, and that the maximum effect is secured by removing excess of the dye. When the most effective conditions for sensitising had been determined, it became possible to compare the sensitising function of a number of *iso*cyanines. As regards the influence of substitution, it appears from comparison of pairs of dyes that the ethyl, methyl, and propyl groups are of equal value; the alkyloxy-group is the most efficient, especially in the quinoline nucleus.

Relation to Light Sensitiveness.

The *iso*cyanines, like the cyanines, are bleached by light. In turpentine the reaction proceeds with a measurable velocity for Auer light. Solutions of equal original absorption were taken, and the times which were required to bleach them to one-third of this were measured. The reciprocal of this was considered as proportional to the light sensitiveness. The issue showed a definite parallelism between light sensitiveness and sensitising power. Although this relation does not hold when comparing different groups of dyes together, and, indeed, it could not be expected to, yet its validity within a group of the same constitution indicates that both phenomena depend on the same photochemical change in the molecule.

Relation between the Sensitising and Absorption Spectra of the Dyes.

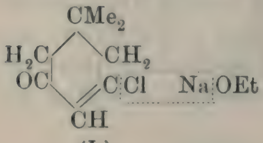
Measurements were made of the sensitising curves for seven of the dyes. They showed that the sensitising maxima depend directly on the maxima in the absorption spectra. The bands are shifted some 10 to 15 $\mu\mu$ toward the red compared with the aqueous absorptions, the α-band near the red being, in general, displaced more than the β-band. Compared with the alcoholic spectrum, the α-band is shifted some 10 $\mu\mu$. This displacement may be considered as coming under Kundt's rule. It is evident that the sensitising maxima can be predicted from the absorption curves, and that structural changes will affect them to the same extent.

The investigations summarised in the foregoing were carried out during the winter and summer semesters of 1906—7 at the Physical Institute of the University of Marburg, to the authorities of which the writer desires to express his thanks for the facilities afforded him, and, in particular, to the Director, Prof. F. Richarz, and to Prof. Karl Schaum for their interest and advice.

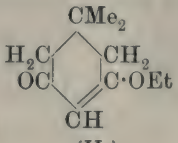
IV.—*Hydroaromatic Ketones. Part I. Synthesis of Trimethyl*cyclo*hexenone* (iso*Phorone*) *and Some Homologues.*

By Arthur William Crossley and Charles Gilling (Salters' Fellow).

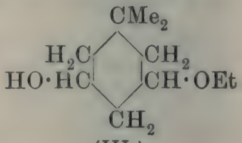
In an account of the action of reducing agents on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (I) (chloroketodimethyltetrahydrobenzene), it has been shown (Trans., 1907, **91**, 63) that when the chloroketone is acted on by sodium in absolute alcoholic solution, a two-fold reaction takes place, the chlorine atom first reacting with the sodium ethoxide formed, with production of the substance having formula (II), which is then reduced to 5-ethoxy-1 : 1-dimethyl*cyclo*hexan-3-ol (III). This unexpected reactivity of the chlorine atom, as exhibited in this reaction,



(I.)



(II.)



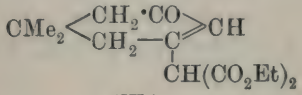
(III.)

seemed to make it of interest to submit chlorodimethyl*cyclo*hexenone to a series of reactions which would throw light on this point, and with this object in view the following experiments were undertaken.

In the first place, chlorodimethyl*cyclo*hexenone was heated with sodium ethoxide in alcoholic solution, when it gave rise, as expected, to the ethyl ether of dimethyldihydroresorcin (II) (Trans., 1899, **75**, 775).

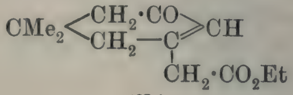
Although interesting from the point of view of this research, the method is not one to be employed for the preparation of this ethyl ether, which can be obtained readily and in almost theoretical amount by the direct esterification of dimethyldihydroresorcin with alcohol and sulphuric acid (Trans., 1908, **93**, 640).

The next reagent tried was ethyl sodiomalonate, which first condenses with chlorodimethyl*cyclo*hexenone with elimination of sodium chloride to give a substance of formula (IV).



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\displaystyle CH(CO_2Et)_2}{\underset{|}{C}}}\end{matrix}\geqslant\mathrm{CH}$$

(IV.)

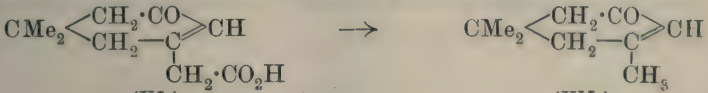


$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\displaystyle CH_2\cdot CO_2Et}{\underset{|}{C}}}\end{matrix}\geqslant\mathrm{CH}$$

(V.)

The reaction does not, however, stop at this stage, for one of the carbethoxy-groups is hydrolysed, probably by the sodium ethoxide, and the resulting carboxyl group loses the elements of carbon dioxide, leaving as reaction product ethyl 1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one-5-acetate (V). This type of reaction is not unusual, and as another example may be quoted the formation of ethyl phloroglucinoldicarboxylate by the interaction of ethyl malonate and ethyl sodiomalonate, where a carbethoxy-group is removed in a similar way (Moore, Trans., 1904, **85**, 165).

Ethyl dimethyl*cyclo*hexenoneacetate is produced to the extent of fifty-five per cent. of the theoretical quantity obtainable from the chlorodimethyl*cyclo*hexenone employed, and its constitution is established by analysis, by the fact that it gives a semicarbazone, and by the nature of the product obtained from it on hydrolysis with alcoholic potassium hydroxide. In the latter case, the free acid (VI) first produced is unstable, and at once loses the elements of carbon dioxide, yielding 1 : 1 : 5-trimethyl-Δ^4-*cyclo*hexen-3-one (VII).



$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\underset{\displaystyle \mathrm{CH_2\cdot CO_2H}}{|}}{C}}\end{matrix}\!\!>\!\mathrm{CH} \quad \longrightarrow \quad \mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\underset{\displaystyle \mathrm{CH_3}}{|}}{C}}\end{matrix}\!\!>\!\mathrm{CH}$$

(VI.) (VII.)

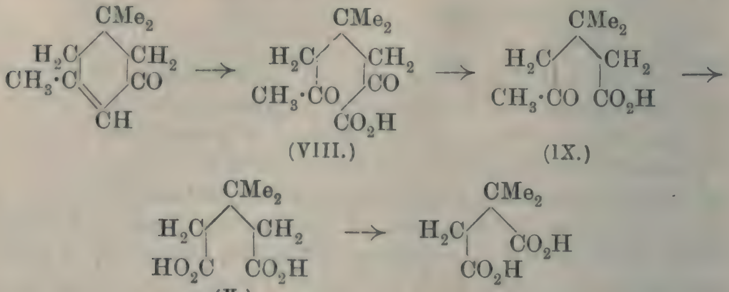
The net result of the action of ethyl sodiomalonate on chlorodimethyl*cyclo*hexenone is, therefore, the replacement of the chlorine atom by a methyl group, and the method of preparation leaves no doubt as to the constitution of the ketone formed.

This is the constitution which has been assigned to *iso*phorone as obtained from the condensation of acetone by Bredt and Rübel (*Annalen*, 1898, **299**, 164) and Kerp and Müller (*ibid.*, 193). Further, Knoevenagel (*ibid.*, 1897, **297**, 185) arrived at the same configuration for the ketone which he synthesised from mesityl oxide and ethyl acetoacetate, and the identity of these ketones with the trimethyl*cyclo*hexenone described in this communication is seen from the following comparison of properties :

	B. p. of ketone.	M. p. of oxime.	M. p. of semicarbazone.
Bredt and Rübel	89°/10 mm.	75° and	—
	100°/17 mm.	99—100°	—
Kerp and Müller	98—100°/16 mm.	76—78°	—
Knoevenagel.........	98°/17 mm. 213—214°/760 mm.	74—75°	186°
Crossley and Gilling ...	99°/18 mm. 214°/754 mm.	78°	190—191°

Bredt and Rübel obtained on oxidation of their ketone with potassium permanganate a crystalline acid, $C_9H_{14}O_4$, a liquid ketonic acid, $C_8H_{14}O_3$, and *as*-dimethylsuccinic acid, and assigned to the two former acids respectively the constitutions represented by formulæ (VIII) and (IX). In the case of the acid $C_9H_{14}O_4$, they proved that it was monobasic, but as it did not form a hydrazone or an oxime, they did not consider the constitution as definitely established. From such an acid, $\beta\beta$-dimethylglutaric acid should be readily obtainable on oxidation, but Kerp and Müller, who treated the ketone with sodium hypobromite, definitely state that they could not find $\beta\beta$-dimethylglutaric acid among the products formed. The oxidation of the ketone described in this communication with potassium permanganate resulted in the isolation of the same products as mentioned by Bredt and Rübel, and as the constitution of the ketone is established by synthesis, it follows that the conclusions of Bredt and Rübel as to the structure of their oxidation products are correct. But, in addition, it is now found that both the acid $C_9H_{14}O_4$ and the acid $C_8H_{14}O_3$ yield ββ-dimethylglutaric acid (X) when oxidised with sodium hypobromite, thus affording additional and direct evidence as to their structure.

Trimethyl*cyclo*hexenone therefore gives a series of oxidation products represented by the following scheme:



(VIII.) (IX.) (X.)

Bredt and Rübel isolated from *iso*phorone two oximes melting respectively at 75° and 99—100°, and suggested, in explanation thereof, that *iso*phorone prepared from acetone is not homogeneous, but contains an isomeric ketone differing only in the position occupied by the double bond, a conclusion also arrived at by Kerp and Müller. Knoevenagel, who prepared *iso*phorone by synthesis from mesityl oxide and ethyl acetoacetate, states that he could only isolate one oxime melting at 75°, whereas Wolff (*Annalen*, 1902, **322**, 380) showed that *iso*phorone prepared by Knoevenagel's method also gives the two oximes mentioned by Bredt and Rübel. In view of these statements, the oxime prepared from the trimethyl*cyclo*hexenone herein described has been subjected to a very thorough process of fractional crystallisation, but no evidence could be obtained of the existence of the oxime melting at 100°, all fractions melting sharply at 78°. Nor is this to be wondered at, for it would not appear possible for the double bond in the ketone to be in any but one position, which fact lends additional support to the suggestion of the other mentioned experimenters, that *iso*phorone prepared from acetone is a mixture of two isomeric ketones.

The condensation of chlorodimethyl*cyclo*hexenone has also been carried out with substituted malonic esters, and the reactions proceed in an analogous manner to that described above, giving rise to homologues of *iso*phorone. Unfortunately, the yields become much smaller as the substituting group increases in molecular weight; thus with ethyl malonate 55 per cent. of the calculated amount of condensation product was obtained; with ethyl methylmalonate, 25 per cent.; with ethyl ethylmalonate, 20 per cent., and with ethyl *iso*propylmalonate, only traces of a condensation product were formed. The ketones are obtained from the initial reaction products on hydrolysis in yields of 70 to 75 per cent. of the calculated quantity.

EXPERIMENTAL.

1. *Interaction of Chlorodimethyl*cyclo*hexenone and Sodium Ethoxide.*

Twelve grams of chlorodimethyl*cyclo*hexenone were added to a solution of 1·8 grams of sodium in 20 c.c. of absolute ethyl alcohol, and heated in a soda-water bottle at the temperature of a boiling-water bath for two hours. The dark reddish-brown reaction product was poured into water, the aqueous liquid extracted four times with ether, the ethereal solution washed with water, dried, and evaporated, when a residue of 10 grams was obtained (82 per cent. of theory) which rapidly solidified. It was crystallised from light petroleum, b. p. 40—60°, after which it melted at 60°, and was found to be identical with the ethyl ether of 1 : 1-dimethyldihydroresorcin previously described (Trans., 1899, **75**, 775).

2. *Interaction of Chlorodimethyl*cyclo*hexenone and Ethyl Malonate.*

Twenty-four grams of chlorodimethyl*cyclo*hexenone (1 molecule) were added to a mixture of 48 grams (2 molecules) of ethyl malonate and 6·9 grams of sodium dissolved in 85 c.c. of absolute alcohol, when a vigorous reaction took place, the liquid turning red, and a solid separating. The reaction product was transferred to two soda-water bottles, which were securely corked, immersed in a water-bath, and heated for two hours, when the whole was poured into water, extracted four times with ether (aqueous solution = *A*), the ethereal solution washed with water, and dried. The residue of 60 grams left on evaporating the ether was distilled in a current of steam so as to remove traces of chlorodimethyl*cyclo*hexenone and excess of ethyl malonate. The residue of the distillation was then extracted five times with ether, the ethereal solution washed, dried, the ether evaporated, and the residual oily liquid distilled under 29 mm. pressure, when the following fractions were collected :

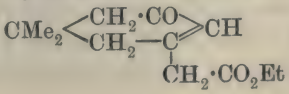
Below 170° = 1 gram. 180—205° = 4·1 grams.
175—180° = 17·5 grams. Residue = 2·8 grams.

The *fraction* 175—180° was redistilled, and a portion boiling constantly was analysed :

0·1637 gave 0·4107 CO_2 and 0·1301 H_2O. C = 68·42 ; H = 8·83.

$C_{12}H_{18}O_3$ requires C = 68·57 ; H = 8·57 per cent.

Ethyl 1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*acetate*,



$$\mathrm{CMe_2}\left<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\overset{|}{CH_2\cdot CO_2Et}}{C}}\end{matrix}\right>\mathrm{CH}\quad ,$$

is a faintly yellow, oily liquid, possessing a slight ethereal odour, and boiling at 171°/22 mm. The yield of pure ester is 55 per cent. of the amount theoretically obtainable from the chlorodimethyl*cyclo*hexenone employed.

The *semicarbazone*, prepared in the usual manner, separated from dilute alcohol in nodules of minute needles melting, after several crystallisations, at 156—157° without decomposition:

0·1094 gave 13·4 c.c. N_2 (moist) at 11° and 754 mm. N = 14·50.

$C_{13}H_{21}O_3N_3$ requires N = 15·72.

$C_{13}H_{21}O_3N_3\cdot\frac{1}{2}C_2H_5\cdot OH$ requires N = 14·48 per cent.

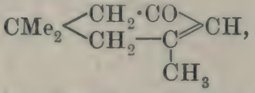
The substance crystallises with half a molecule of ethyl alcohol, as confirmed by a determination of carbon and hydrogen.

*Hydrolysis of Ethyl Dimethyl*cyclo*hexenoneacetate.*—Fifty-one grams of ethyl dimethyl*cyclo*hexenoneacetate (1 molecule) were added to an alcoholic solution of 34 grams (2·5 molecules) of potassium hydroxide and heated on the water-bath for two hours. The mixture, which rapidly turned red and from which a solid separated, was poured into water, acidified with sulphuric acid, when a rapid evolution of carbon dioxide occurred, and extracted four times with ether. The ethereal solution was washed, first with a dilute solution of sodium hydroxide, then with water, dried, and, after evaporating the ether, the residue was distilled under a pressure of 24 mm., when 25·5 grams (76 per cent. of theory) passed over at 102·5—103°. This portion was analysed after a second distillation:

0·1291 gave 0·3694 CO_2 and 0·1224 H_2O. C = 78·04; H = 10·53.

$C_9H_{14}O$ requires C = 78·26; H = 10·14 per cent.

1 : 1 : 5-*Trimethyl*-Δ^4-cyclo*hexen-3-one*,



$$\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{C}}}\end{matrix}{>}\mathrm{CH},$$

is a colourless, refractive liquid, possessing an agreeable slightly camphoraceous odour, and boiling at 99°/18 mm., 109°/32 mm., and 214°/754 mm.

The *semicarbazone* crystallises from alcohol in radiating clusters of flattened needles, melting to a clear liquid at 190—191°, and giving off gas at 195° (Knoevenagel gives the melting point 186°):

Found, N = 21·47. $C_{10}H_{17}ON_3$ requires N = 21·54 per cent.

The *oxime* was prepared by dissolving 2 grams of hydroxylamine hydrochloride in the smallest possible quantity of water, adding absolute alcohol, then 2 grams of the ketone, and neutralising the solution with potassium hydroxide. After two days, the whole was poured into brine, extracted four times with ether, the ethereal solution washed, dried, and the ether evaporated, when an oily residue was left which rapidly solidified. The solid was spread on porous plate, and crystallised from light petroleum (b. p. 40—60°), when it separated in large, transparent prisms melting at 78°:

Found, N = 9·08. $C_9H_{15}ON$ requires N = 9·15 per cent.

A quantity of the oxime prepared according to the directions given by Bredt and Rübel was fractionally crystallised from light petroleum, but, although a large number of fractions were obtained, they all melted in the neighbourhood of 78°, and no evidence of the presence of a higher melting oxime could be obtained.

*Oxidation of Trimethyl*cyclo*hexenone.*—Twenty grams of the ketone were suspended in 150 c.c. of water, and a 4 per cent. solution of potassium permanganate was slowly added, care being taken to maintain the whole at the temperature of melting ice. Oxidation was complete when 64 grams of potassium permanganate had been used, and, after working up in the usual manner, the residual yellow oil, weighing 24 grams, was distilled under 33 mm. pressure and the following fractions collected:

Below 150° = 1 gram. 160—170° = 3·2 grams.
150—160 = 3·6 grams. 170—190° = 2·2 grams.
190—250° = 10·2 grams.

The first four fractions were redistilled under 30 mm. pressure and separated into two main portions boiling at 150—160° and 160—165°.

The *fraction* 150—160°/30 mm., on standing, deposited minute needles which, after crystallisation from water, melted at 141°, nor was this melting point altered on mixing with pure *as*-dimethylsuccinic acid. The identity of these two substances was further proved by the preparation of an anilic acid which melted at 185—186° (*as*-dimethylsuccinanilic acid melts at 186°).

The *fraction* 160—165°/30 mm. was again distilled, and a portion boiling at 160°/29 mm. analysed:

0·1191 gave 0·2622 CO_2 and 0·0935 H_2O. C = 60·04; H = 8·73.
$C_8H_{14}O_3$ requires C = 60·76; H = 8·86 per cent.

Although the analytical numbers do not agree very closely with theory, probably due to the presence of traces of dimethylsuccinic acid, they are sufficiently good to show that this liquid must be γ-acetyl-$\beta\beta$-dimethylbutyric acid, $CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (compare Bredt and Rübel), described by Vorländer (*Annalen*, 1899, **304**, 19). This was further established by preparing from the acid a semicarbazone, which crystallised from alcohol in flattened needles melting at 168° with evolution of gas:

Found, N = 19·42. $C_9H_{17}O_3N_3$ requires N = 19·53 per cent.

The *fraction* 190—250°/33 mm. yielded on redistillation 6·5 grams of a viscid liquid boiling at 220—245°/30 mm., which solidified with difficulty, and the solid crystallised from benzene in beautiful triangular plates melting at 98—99°:

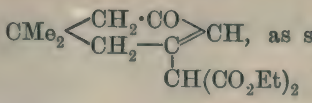
0·1104 gave 0·2351 CO_2 and 0·0766 H_2O. C = 58·08; H = 7·71.
$C_9H_{14}O_4$ requires C = 58·06; H = 7·53 per cent.

This acid is identical with the γγ-dimethyl-αε-diketoheptoic acid, $CO_2H·CO·CH_2·CMe_2·CH_2·CO·CH_3$, described by Bredt and Rübel, who were unable to prepare from it a hydrazone or an oxime. The present authors were equally unsuccessful in attempting to isolate a semicarbazone.

Oxidation of the Acid, $C_8H_{14}O_3$.—Nine grams of the acid were dissolved in 100 c.c. of water containing a slight excess of sodium hydroxide, and bromine added drop by drop, the liquid being maintained colourless and slightly alkaline by the addition of more sodium hydroxide from time to time. When the addition of bromine caused a permanent yellow coloration, which persisted even on the addition of a little more sodium hydroxide, the oxidation was stopped, and the separated bromoform removed by extraction with ether. Sodium hydrogen sulphite was then added in sufficient quantity to destroy the excess of sodium hypobromite, the liquid evaporated to a small volume, acidified with sulphuric acid, and extracted ten times with ether. The ethereal solution was washed with a solution of sodium sulphite to remove bromine, then with water, dried, and the ether evaporated, when 6·5 grams of solid were obtained. This residue was heated with acetyl chloride for two hours, the solvent evaporated, and the residue crystallised from benzene, when it melted at 125°. This is the melting point of ββ-dimethylglutaric anhydride, and the identity of the two substances was further established by converting a portion into the corresponding acid, which melted at 100—101°, nor was this melting point lowered by mixing with an equal quantity of pure ββ-dimethylglutaric acid:

0·1287 gave 0·2479 CO_2 and 0·0900 H_2O. C = 52·53; H = 7·77.
$C_7H_{12}O_4$ requires C = 52·50; H = 7·50 per cent.

Oxidation of the Acid $C_9H_{14}O_4$.—Six and a-half grams of this acid were oxidised with sodium hypobromite exactly as described above, when 5·5 grams of a solid residue were obtained. After treatment with acetyl chloride and crystallisation from benzene, the anhydride melted at 124° and the corresponding acid at 100—101°, nor were these melting points altered on admixture with pure ββ-dimethylglutaric anhydride and acid respectively.

The *fraction* 180—205° (see p. 23), weighing 4·1 grams, consisted of a mixture of ethyl dimethyl*cyclo*hexenoneacetate and the corresponding dicarboxylic ester,  $CMe_2<\begin{matrix}CH_2\cdot CO\\ CH_2-\underset{\substack{|\\ CH(CO_2Et)_2}}{C}\end{matrix}>CH$, as seen from the following analysis :

0·1365 gave 0·3334 CO_2 and 0·1069 H_2O. C = 66·61 ; H = 8·70.

$C_{12}H_{18}O_3$ requires C = 68·57 ; H = 8·57 per cent.
$C_{15}H_{22}O_5$,, C = 63·83 ; H = 7·80 ,,

Further, when hydrolysed in the manner already described with alcoholic potassium hydroxide, it yielded only trimethyl*cyclo*hexenone.

The *residue* (see p. 23) was a resin, from which, by extraction with light petroleum (b. p. 80—100°), a small amount of a white solid was obtained crystallising from methyl alcohol in silky needles melting at 158°, but the amount was too small for complete investigation.

The aqueous alkaline liquid *A* (see p. 23) was acidified with sulphuric acid and extracted four times with ether. On evaporation, the ethereal solution yielded 2·3 grams of a white solid crystallising from dilute alcohol in white, feathery needles melting at 141°.

For a long time it was not found possible to suggest a formula for this substance, as it was naturally thought to contain only carbon, hydrogen, and oxygen. In reality, it contains nitrogen also, and its formation is due to the fact that the ethyl malonate used contained appreciable quantities of ethyl cyanoacetate. Indeed, when this latter ester is employed instead of ethyl malonate in the original condensation, the substance melting at 141° becomes the main reaction product, and its exact nature is at present under investigation.*

3. *Interaction of Chlorodimethyl*cyclo*hexenone and Ethyl Methylmalonate.*

Fifty-two grams of ethyl methylmalonate (2 molecules), prepared according to the directions given by Perkin (Trans., 1896, **69**, 1477), were mixed with a solution of 6·9 grams of sodium in 85 c.c. of absolute alcohol, 24 grams of chlorodimethyl*cyclo*hexenone added, and the whole worked up exactly in the manner described on p. 23. The crude substance, after two distillations under 30 mm. pressure, gave the fractions : 174—180°, 9·1 grams ; 180—210°, 2·6 grams.

The *fraction* 174—180° was redistilled, and a constant boiling portion analysed :

0·0982 gave 0·2500 CO_2 and 0·0825 H_2O. C = 69·43 ; H = 9·33.

$C_{13}H_{20}O_3$ requires C = 69·64 ; H = 8·93 per cent.

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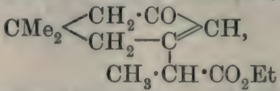
* The ethyl malonate used in these experiments was purchased from Messrs. Kahlbaum, who inform us that it is practically impossible to prepare ethyl malonate directly from cyanoacetic acid so as to be entirely free from ethyl cyanoacetate. The firm will, however, shortly place on the market ethyl malonate free from nitrogen under the name : ethyl malonate "Kahlbaum."

Ethyl a-1:1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*propionate*,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\mathrm{CH_3\cdot CH\cdot CO_2Et}}{C}}\end{matrix}\gg\mathrm{CH},$$

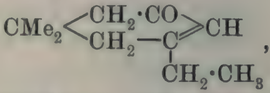
is a colourless, refractive liquid, boiling at 180°/33 mm., and possessing a fatty odour resembling that of castor oil.

The *fraction* 180—210° consisted doubtless of a mixture of the preceding ester and the corresponding dicarboxylic ester, for on hydrolysis with alcoholic potassium hydroxide it yielded the dimethylethyl*cyclo*hexenone described below.

*Hydrolysis of Ethyl Dimethyl*cyclo*hexenonepropionate.*—Fifteen grams of the ester were hydrolysed with 10 grams of potassium hydroxide, and, after working up in the manner described, the reaction product was distilled under 30 mm. pressure, when nearly the whole (7·5 grams) boiled between 123—124°. After a second distillation, it was analysed:

0·1058 gave 0·3050 CO_2 and 0·1037 H_2O. C = 78·62; H = 10·88.
$C_{10}H_{16}O$ requires C = 78·94; H = 10·53 per cent.

1:1-*Dimethyl*-5-*ethyl*-Δ^4-cyclo*hexen*-3-*one*,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\mathrm{CH_2\cdot CH_3}}{C}}\end{matrix}\gg\mathrm{CH},$$

is a colourless, refractive liquid, boiling at 122°/29 mm., and possessing a pleasant camphoraceous odour.

The *semicarbazone*, prepared in the usual manner, crystallised from dilute alcohol in flattened needles which, after several crystallisations, melted at 197° with evolution of gas:

0·1040 gave 18·7 c.c. N_2 (moist) at 752 mm. and 19·5°. N = 20·38.
$C_{11}H_{19}ON_3$ requires N = 20·10 per cent.

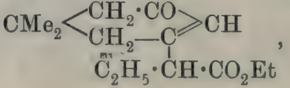
4. *Interaction of Chlorodimethyl*cyclo*hexenone and Ethyl Ethylmalonate.*

Fifty-five grams of ethyl ethylmalonate, 6·9 grams of sodium in 85 c.c. of absolute alcohol, and 24 grams of chlorodimethyl*cyclo*hexenone were employed in this experiment. The resulting liquid was distilled at 32 mm. pressure, when 7·1 grams, boiling at 180—190°, and 1·5 grams, boiling at 190—220°, were obtained.

The *fraction* 180—190° was redistilled and analysed:

0·1019 gave 0·2627 CO_2 and 0·0870 H_2O. C = 70·30; H = 9·48.
$C_{14}H_{22}O_3$ requires C = 70·59; H = 9·24 per cent.

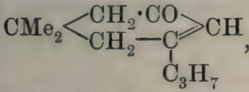
Ethyl a-1:1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*butyrate*,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\mathrm{C_2H_5\cdot CH\cdot CO_2Et}}{C}}\end{matrix}\gg\mathrm{CH},$$

is an almost colourless oily liquid, boiling at 185°/30 mm., and possessing a fatty odour.

The *fraction* 190—220° corresponds with the similar boiling portion obtained in the preparation of the lower members of this series of esters. It is doubtless a mixture of the monocarboxylic and dicarboxylic esters, for on hydrolysis it yielded the dimethylpropyl*cyclo*hexenone described below.

*Hydrolysis of Ethyl Dimethyl*cyclo*hexenonebutyrate.*—This was carried out as with the preceding esters, when 70 per cent. of the theoretical amount of 1 : 1-*dimethyl*-5-*propyl*-Δ^4-cyclo*hexen*-3-*one*,  $\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH_2\cdot CO}\\ \mathrm{CH_2-\underset{\displaystyle C_3H_7}{C}}\end{matrix}{>}\mathrm{CH}$, was obtained as a colourless liquid, boiling at 125°/19 mm., and possessing an agreeable camphoraceous and celery-like odour :

0·1146 gave 0·3340 CO_2 and 0·1129 H_2O. C = 79·49 ; H = 10·94.

$C_{11}H_{18}O$ requires C = 79·52 ; H = 10·84 per cent.

The *semicarbazone* crystallised from dilute alcohol in rosettes of flattened needles, melting at 156° with slight decomposition, and giving off gas at 190° :

0·1047 gave 16·8 c.c. N_2 (moist) at 753 mm. and 13°. N = 18·77.

$C_{12}H_{21}ON_3$ requires N = 18·83 per cent.

Attempts to effect the condensation of chlorodimethyl*cyclo*hexenone and ethyl *iso*propylmalonate were also made, but, although traces of an ester were obtained, the yield was so small as to render the method of no practical utility as a means of obtaining the higher members of this series of hydroaromatic ketones.

The authors take this opportunity of expressing their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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V.—*The Decomposition of Carbon Dioxide by the Silent Electric Discharge.*

By ALFRED HOLT, jun.

IN 1885 Shenstone described an experiment * to the Physical Society which illustrated the changes that occur in the nature of an electric discharge passing between parallel glass plates.

When the glass surfaces were about 1 cm. apart, the discharge consisted of a few large sparks like those produced by an induction coil. On diminishing the distance between the plates, the sparks became more numerous.

When the distance between the plates was about 1 mm., the sparks became fewer, and a glow made its appearance. If the air between the plates was moist, the glow vanished and the sparks reappeared.

A similar change was observed in the discharge when oxygen was substituted for air, but the glow was feebler.

The investigations of Lenard on the chemical effects brought about by ultra-violet light (*Ann. Physik*, 1900, **70**, 486), and the researches undertaken by many experimenters with induction sparks, point to the conclusion that the silent discharge acts by reason of ultra-violet light as well as by the heating effects produced by the sparks occurring under certain conditions.

Since the decomposition of moist and dry carbon dioxide both by sparks and ultra-violet light has been investigated, it seemed to the author that a study of the action of the silent discharge on this gas would throw additional light on the nature of the discharge itself.

Brodie has shown that carbon dioxide dried over sulphuric acid is decomposed into carbon monoxide and oxygen, and that a very large proportion of the oxygen thus produced is ozonised (*Phil. Trans.*, 1874, **164**, 83).

The action of sparks has been examined by several authors, particularly by Dixon (Trans., 1885, **47**, 571) and Collie (Trans., 1901, **79**, 1063). Their results show that the gas is decomposed whether moist or dry, and that the shorter the spark and the lower the pressure of the gas the larger is the amount decomposed.

Chapman, Chadwick, and Ramsbottom (Trans., 1907, **91**, 942), in studying the chemical action of ultra-violet light, found no action on moist carbon dioxide; the dry gas, however, was decomposed to an extent which varied inversely with the pressure.

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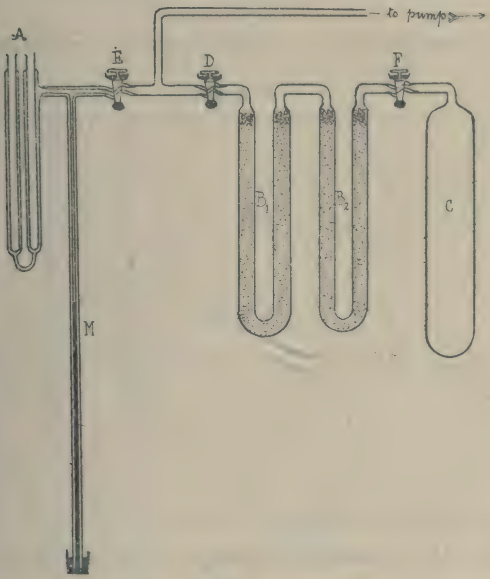
* This experiment is described at the end of a paper published in conjunction with Cundall (Trans., 1887, **51**, 610).

In the present research, only the amounts of carbon monoxide and oxygen produced in the decomposition were determined, the apparatus employed proving unsuitable for the estimation of the ozone. The oxygen was always found to be more or less ozonised. In a future communication, the author hopes to give some details concerning the amount of ozone produced during the decomposition of carbon dioxide by the silent electric discharge under varying conditions of pressure and dryness.

The apparatus employed in the present investigation is illustrated in Fig. 1.

FIG 1.



The carbon dioxide was obtained by heating pure sodium hydrogen carbonate in the vessel *C*; B_1 and B_2 were long **U**-tubes filled with phosphoric oxide; *A* was the ozoniser; *M* a manometer. The tubes containing the phosphoric oxide were removed during the experiments with moist gas, but the apparatus was otherwise unaltered. In the experiments with the dry gas, a drop of sulphuric acid was placed on the top of the mercury column in the manometer in order to protect the bright surface of the mercury from the action of ozone. When experimenting with the moist gas, a drop of water replaced the sulphuric acid, as it served both to protect the surface of the mercury and to saturate the gas with water vapour.

The method of carrying out an experiment was as follows: the whole apparatus was evacuated, the tap *D* was shut, and B_1 and B_2 filled with carbon dioxide. The tap *F* was then closed, and the gas allowed to dry in contact with the phosphoric oxide for at least twelve hours.

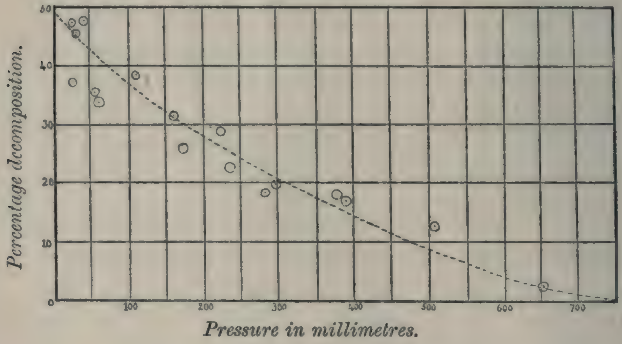
The tap *D* was now opened, and the gas passed into the ozoniser, the pressure being read on the manometer. The taps *E* and *D* were shut, and the space between them and the pump evacuated.

The silent discharge was passed through the gas in the ozoniser until the pressure, as indicated by the manometer, became constant. The tap *E* was then opened, and the gas pumped out and analysed.

The decomposition of dry carbon dioxide is shown by the curve in Fig. 2. The amount of gas decomposed varied inversely as the pressure.

The actual decomposition at any one pressure varied, alterations in the degree of dryness of the gas and intensity of the discharge producing considerable changes. As a result of a large number of experiments, the greatest percentage of carbon dioxide is decomposed when the gas has been very carefully dried and the discharge is strong.

FIG. 2.



Similar experiments were carried out with ozonisers, in which the annular space through which the discharge passed varied from 0·5 mm. to 5 mm. in breadth.

It was found, *ceteris paribus*, that the narrower the space the greater is the decomposition.

The numbers given below were obtained in one series of experiments, in which the gas was as far as possible of uniform dryness and the discharge of constant intensity.

Pressure in mm.	30	60	165	235	300	388	652
Percentage decomposition ...	48·4	35·9	31·0	21·8	19·9	16·4	2·6

Entirely different results were obtained with the moist gas, the decomposition becoming greater as the pressure increased.

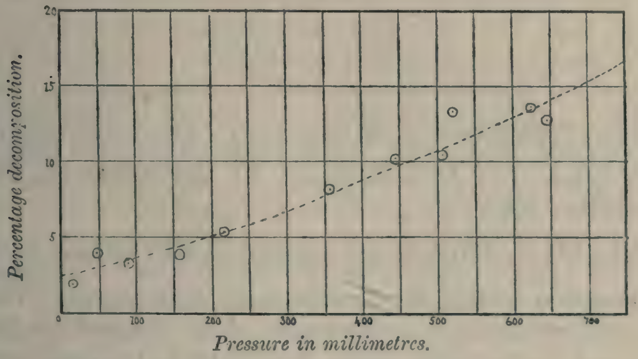
The following numbers show the actual amount of decomposition recorded in one series of experiments, the curve in Fig. 3 representing the mean of all the values obtained for different pressures.

Pressure in mm.	50	85	220	355	448	525	628
Percentage decomposition ...	3·8	4·0	5·5	8·1	10·3	13·5	14·0

As in the case of the dry gas, a weak discharge, or the use of an ozoniser with a wide annular space, diminished the amount of decomposition.

An examination of the results shows that dry carbon dioxide is decomposed by the silent discharge to about the same extent as by sparks or ultra-violet light, but that the moist gas decomposes quite differently.

FIG. 3.



Two explanations can be given of the behaviour of the moist gas, one resulting from the interaction of the decomposition products, the other from changes occurring in the nature of the discharge itself.

If the following series of reactions took place in moist carbon dioxide to an extent varying inversely with the pressure of the gas, the decomposition would be greater as the pressure increased.

$$2CO_2 = 2CO + O_2$$
$$3O_2 = 2O_3$$
$$O_3 + CO = CO_2 + O_2.$$

But Remsen and Southworth (*Ber.*, 1875, 8, 1414) have shown that ozone and carbon monoxide do not react together under varying conditions, and the author has also carried out some experiments with these gases at diminished pressures and obtained negative results; it would seem, therefore, that this cycle of reactions does not take place to any appreciable extent. Changes taking place in the discharge itself afford the simplest explanation of the behaviour of the moist gas.

It seems probable that in the moist gas the discharge at low pressures consists almost entirely of ultra-violet light, but as the pressure increases, more and more sparks occur in the discharge, and bring about the decomposition of the gas.

The changes which Shenstone observed when the discharge passed through a moist atmosphere are exactly in accordance with this view, the sparks becoming more numerous in a wet gas and with increasing pressure.

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VI.—*The Absorption Spectra of para-Benzoquinone, Quinol, and Quinhydrone in the State of Vapour and in Solution.*

By WALTER NOEL HARTLEY AND ALFRED GODFREY GORDON LEONARD.

THE absorption spectra of *p*-benzoquinone, its mono- and di-oximes, and its chloroimide and dichloroimide were examined by Hartley, Dobbie, and Lauder (*Brit. Assoc. Report*, 1902, 107), and compared with the various structural formulæ which had been proposed for these substances.

The spectra of *p*-benzoquinone were found to differ widely from those of its derivatives, but it was difficult to form a decided opinion whether this was due merely to a difference in composition or to some definite structural difference. A comparison of the curves of *p*-benzoquinonechloroimide and *p*-nitrosophenol, which substances differ by substitution for a hydrogen atom, of chlorine in the one case, and of hydroxyl in the other, was expected to disclose such a resemblance or a difference between them as might be observed between *p*-benzoquinonedichloroimide and *p*-benzoquinonedioxime; the difference proved to be much greater in the one case than in the other, so much so that it did not favour the representation of *p*-nitrosophenol (*p*-benzoquinoneoxime) by a formula similar to that of *p*-benzoquinonechloroimide. Hence, it would appear that the absorption phenomena are complicated probably by the dynamic isomerism of the *iso*nitroso-complex. In general terms, it may be said that *p*-nitrosophenol yields a curve showing two absorption bands; *p*-benzoquinonechloroimide differs from this by its curve showing one band only; the dichloroimide has one band, the dioxime also one, but it is of greater width and intensity than that of the dichloroimide.

The powerful oxidising properties of *p*-benzoquinone when submitted to the action of light in presence of polyhydric aliphatic alcohols and of ethyl alcohol in particular were referred to, and alcohol was considered unsuitable as a solvent for *p*-benzoquinone, because of its liability to reduce this substance to quinol (Ciamician and Silber, *Ber.*, 1901, **34**, 1350). On that account, the solutions of *p*-benzoquinone then already examined had been prepared with water.

Experiments with an aqueous solution of *p*-benzoquinone prepared in a dark room were repeated by one of us in the year 1902, subsequent to the publication of the Report mentioned, and it was found that the action of light speedily changed the colour of the liquid from yellow to brown, which was deemed to be evidence of a decisive change in chemical composition, leading to the production of some substance not pre-existing in the solution. From a comparison of the curves for *p*-benzoquinone and quinol, it was believed that quinol was produced.

Baly and Stewart (Trans., 1906, **89**, 506) regard water as an unsatisfactory solvent, because it is a substance wi h strong residual affinity, and in the examination of organic substances it is the influence or properties of residual affinity which is the subject of investigation. They point out that the absorption curve of *p*-benzoquinone in alcoholic solution is entirely different from that observed by Hartley, Dobbie, and Lauder in the aqueous solution. The examination of more highly concentrated alcoholic solutions showed an absorption band lying between $^1/\lambda$ 1950 and 2800, which they term the isorropic band. As regards the aqueous solution, they say that apparently an additive product is formed; the isorropic band shrinks, and a benzenoid band makes its appearance at $^1/\lambda$ 4000. Thus there are three bands in the absorption spectrum of *p*-benzoquinone in aqueous solution.

These results are in agreement with the unpublished observations referred to above as being made in the year 1902. It was, however, seen that there is a great probability that both the alcoholic and aqueous solutions of *p*-benzoquinone yield quinol, and that the band of quinol appears as the second band in these spectra. Further work in this direction was held in abeyance until the completion of experiments on the absorption spectra of substances in the state of vapour.

PART I.

The Absorption Spectrum of p-*Benzoquinone Vapour at Different Temperatures.*

As the effect of different solvents appears to lead to a change in the absorption spectrum of *p*-benzoquinone, and because the colour of the compound is remarkable, it became desirable that we should ascertain the absorption spectrum of the substance itself, to what extent the colour was due to any very definite absorption band, and, furthermore, to show the relationship between the spectrum of the substance in a state of vapour and in solution in an inert solvent.

EXPERIMENTAL.

The spectra of the vapour were obtained by means of the tube apparatus employed in examining the vapour spectra of benzene and its homologues at different temperatures and pressures, but the flask for liquids was removed (*Phil. Trans.*, 1908, *A*, **208**, 475). A weighed quantity of pure crystallised *p*-benzoquinone was introduced into the tube, and gradually vaporised by raising the temperature. Exposures were made at definite intervals, during which the temperature of the bath was kept constant, and the pressure inside the tube after heating allowed to attain to atmospheric pressure. In case any gas might be present which could act chemically on the vapour, pure dry carbon dioxide was passed through the apparatus to expel all air, and further operations were performed in this neutral gas.

In two series of spectra there were twenty-seven bands in all, although at no one temperature between 17° and 147° were more than eight bands visible.

The *p*-benzoquinone weighed 0·0094 gram; it was contained in a tube, 150 mm. in length, which was filled with dry carbon dioxide. The whole of the substance could not have been entirely vaporised at 70°. The numbers bracketed represent wave-lengths on each side of a band. Where there is but one measurement, the band is narrow.

SERIES I.

17°.	30°.	42°.	52°.	70°.
λ.	λ.	λ.	λ.	λ.
2380 } 76 }	2419	2456 } 49 }	2505 } 01 }	2527·5
75 } 70 }	2416 } 13 }	38 } 29·5 }	2499·5 } 96 }	2523 } 21 }

SERIES I—(*continued*).

17°.	30°.	42°.	52°.	70°.
λ.	λ.	λ.		λ.
54 48·5	08 06	22·5 19		05·5 01
47·5 43·5	2399·5 91·5	16 14		2499·5 96
	80·5 76			
	75 70			
	59 54·5			
	54 50			
4 bands	8 bands	4 bands	2 bands	4 bands

SERIES II.

The weight of *p*-benzoquinone was 0·0726 gram, and with this larger quantity the whole of the crystals were not vaporised until the temperature of 147° had been attained. As before, the atmosphere of the tube was carbon dioxide.

Abbreviations.—*d.* Diffused ; *f.* faint ; *sh.* sharp ; *s.* strong ; *b.* broad.

63°.	86°.	111°.	147°.
λ.	λ.	λ.	λ.
2888 79 *f. d.*	4341 20 *sh. f.*	4343·5 23 *sh. s.*	4383 21 *s.*
53 39·5 *d.*	2959 54 *d.*	3038 31 *s.*	4270 44
	2882·5 78·5 *d.*	3022 2991 *f.*	4161 015 *b. s.*
	73·5 62·5 *d.*		3789 49 *f.*
	50 40		3051·5 31 *s.*
2 bands	5 bands	3 bands	5 bands

General Remarks.—In the spectra at the lower temperatures and with the smaller weight of *p*-benzoquinone, it will be observed that all the bands are situated in the most refrangible rays beyond λ 2600. Beyond the bands there is a general absorption, which increases in extension with rise of temperature into the region of less refrangible rays; at the same time, other bands make their appearance.

In Series II, where the quantity of substance was nearly eight times as large, and the temperature finally attained was 147°, the changes are of the same nature, that is to say, the general absorption creeps up with rise of temperature into the less refrangible rays, and at the same time new bands develop.

The Absorption Spectrum of Quinol Vapour at Different Temperatures in an Atmosphere of Hydrogen containing Alcohol Vapour.

0·0081 Gram of quinol was heated in the metal tube, but was not all vaporised. The quinol was quite pure, consisting of colourless crystals which had undergone no change in properties after condensation from the vaporous state. No *p*-benzoquinone was formed.

Abbreviations.—*f.* Faint; *s.* strong; *v.s.* very strong.

Temperature.	I. *Absorption band* at	II. *Absorption band.*		Rays transmitted to
	λ.	λ.	λ.	λ.
70°	2538 *f.*	2396 to	2332	2144·5
80	2538 *f.*	2402 ,,	2334	2144·5
90	2538 *f.*	2425 ,,	2321	2144·5
100	2538 *v.s.*	—	—	2430
110	2538 *v.s.*	—	—	2435
		III. *Absorption band.*		
		λ.	λ.	
120	2538 *s.*	2949 to	2680	2442
130	2538 *v.s.*	2949 ,,	2680	2449
140	2538 *v.s.*	3011 ,,	2680	2496
150	2538 *s.*	3039 ,,	2647	2510
160	2538 *v.s.*	3066 ,,	2575	2530
170	2538 *f.*	3080 ,,	2575	2538
175	—	3080 ,,	2575	—

The spectrum is characterised by (1) a very narrow, but well-defined, absorption band at λ 2538; (2) a broad band ranging from λ 2396 to 2332 at 70°, and (3) one from λ 3080 to 2575 at 170°. The second band, with its centre at λ 2364, is not well shown when the solid is vaporised in air or carbon dioxide, but it appears when the quinol is vaporised in hydrogen, and more strongly when the hydrogen is mixed with alcohol vapour.

It would appear from this that the band is really a quinol band.

On examining the spectrum of pure quinol in aqueous solution, it is seen that there is a weakening at this part of the spectrum; in fact, a feeble absorption, but no well-defined band. The band at λ 2538 is more persistent in this series of photographs than in those taken from quinol vaporised either in air or in carbon dioxide, probably owing to the decreased extent of the general absorption under the former conditions. Special measurements were made of this band when the quinol was vaporised in air. At different temperatures above 100°, it becomes very strong and broader,

Measurements of the Fine Band in the Absorption Spectrum of Quinol Vaporised in Air.

Abbreviations.—f. Faint; *s.* strong; *v.s.* very strong.

22°.	50°.	100°.	110°.	120°.	130°.
λ.	λ.	λ.	λ.	λ.	λ.
2538 *f.*	2538 *f.*	2538 *s.*	2538 *v.s.*	2539 *v.s.*	2539 *v.s.*
—	2538	2538	3537·5	2537	2537·5

At 140° the band becomes merged in a general absorption. It will be seen that the band extends slightly on *both sides* as the temperature rises; in this respect it differs from the vapour bands of the hydrocarbons. Where two numbers are bracketed, it means that micrometer measurements were made on each side of the band, but if the numbers are the same, it means that the band was too narrow to make a difference in linear measurements equivalent to 1 Ångström unit.

The Absorption Spectrum of Quinhydrone Vapour in Air at Different Temperatures.

The weight of quinhydrone taken was 0·05 gram; this was not entirely vaporised, but the vapour condensed was apparently quite unchanged. The fine, but very narrow, absorption band characteristic of quinol vapour at λ 2538, which is observed as faint at 22° and strong at 100°, did not appear. It might have been expected that it would be photographed if the substance underwent dissociation when vaporised; it is therefore inferred that dissociation did not take place. The broader quinol band commencing about λ 2900 does not appear very strongly, but this may be explained by the increased intensity of the general absorption hereabouts.

Temperature.	*Absorption band.*		Rays transmitted to
	λ.	λ.	λ.
18°	—	—	2144·5
40	2373 to	2332	2144·5
50	2401 ,,	2332	2144·5
60	2425 ,,	2332	—
70	2430 ,,	2321	2144·5
80	—	—	2430
90	—	—	2456
100	—	—	2469
110	—	—	2474
	* Rays weak from		
	λ.	λ.	λ.
120	2949 to	2568	2544
130	2973 ,,	2573	2572
140	Rays weak beyond 2973		2572
150	—		3073
160	—		3073
170	—		3073

* This feeble absorption corresponds with the principal band of quinol, but it is somewhat narrower, see p. 38, at temperatures 120° to 140°.

PART II.

The Absorption Spectra of Solutions of p-*Benzoquinone, Quinol, and Quinhydrone.*

p-*Benzoquinone.*—This was prepared by resubliming a fine specimen procured from Kahlbaum ; it was obtained in feathery groups of large crystals.

The solutions were all prepared in the dark room and exposed to red light only. Past experience of one of us has shown that it is necessary to photograph the spectra immediately after the solutions have been prepared, and to record the concentration and thickness of the layers of solution examined.

p-*Benzoquinone in Absolute Alcohol.*—Five different solutions were prepared, and series of spectra photographed on five different plates, but they are all comprised in a series of twenty-four spectra on one plate. The tabulated statement below shows the concentration of the different solutions prepared and the thicknesses through which the photographs were taken.

5 milligram-mols. in 100 c.c. ...	100	70	50	40	30	20 mm.				
1 milligram-mol. in 100 ,, ...	50	40	30	20	10	5	4	3	2	1 mm.
1 ,, ,, 2500 ,, ...	20	15	10	5	4	3	2	1 mm.		

p-*Benzoquinone in Water.*—The freshly-prepared aqueous solutions were of the same concentrations, and examined through the same thicknesses as above.

In the case of the aqueous solution which had been kept for eight days exposed freely to daylight, the concentration of 1 milligram-mol. in 100 c.c. was examined and diluted with water to 500 c.c.

1909.

International Atomic Weights.

		O=16.			O=16.
Aluminium	Al	27·1	Molybdenum	Mo	96·0
Antimony	Sb	120·2	Neodymium	Nd	144·3
Argon	A	39·9	Neon	Ne	20
Arsenic	As	75·0	Nickel	Ni	58·68
Barium	Ba	137·37	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·0
Cæsium	Cs	132·81	Platinum	Pt	195·0
Calcium	Ca	40·09	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·6
Cerium	Ce	140·25	Radium	Ra	226·4
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·1	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·5	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·4	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·62
Gallium	Ga	69·9	Sulphur	S	32·07
Germanium	Ge	72·5	Tantalum	Ta	181·0
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·0	Thallium	Tl	204·0
Hydrogen	H	1·008	Thorium	Th	232·42
Indium	In	114·8	Thulium	Tm	168·5
Iodine	I	126·92	Tin	Sn	119·0
Iridium	Ir	193·1	Titanium	Ti	48·1
Iron	Fe	55·85	Tungsten	W	184·0
Krypton	Kr	81·8	Uranium	U	238·5
Lanthanum	La	139·0	Vanadium	V	51·2
Lead	Pb	207·10	Xenon	Xe	128
Lithium	Li	7·00	Ytterbium (Neoytterbium)	Yb	172
Lutecium	Lu	174	Yttrium	Y	89·0
Magnesium	Mg	24·32	Zinc	Zn	65·37
Manganese	Mn	54·93	Zirconium	Zr	90·6
Mercury	Hg	200·0			

and to 2,500 c.c.; the thicknesses examined were 50, 40, 30, 20, 15, 10, and 5 mm.

p-*Benzoquinone in Anhydrous Ether.*—In addition to the concentrations and thicknesses of solution being the same as those of the alcoholic solutions, a series of photographs and also eye observations with the spectroscope were made on a solution of 25 milligram-mols. in 100 c.c. at thicknesses of 100, 70, 50, 40, 30, 20, 10 mm.

Quinol in Water.—The absorption curves of this substance having been drawn and described previously, only the following solutions were examined:

1 milligram-mol. in 100 c.c....	40	30	20	10	5	4	3 mm.
1 ,, ,, 2500 ,, ...	50	40	30	20	10	5	4 ,,

Quinhydrone in Water.—The concentrations prepared were the same as for quinol, but the thicknesses of liquid examined differed; these were respectively for the former and the latter:

	50	40	30	20	10	5	4	3	2	1 mm.
and	20	15	10	5	4	3	2	1 mm.		

Quinhydrone in Alcohol.—

5 milligram-mols. in 100 c.c. ...	100	70	50	40	30	20	10 mm.		
1 milligram-mol. in 100 ,, ...	40	30	20	10	5	4	3	2	1 mm.
1 ,, ,, 2500 ,, ...	20	15	10	5	4	3	2	1 mm.	

When freshly-dissolved in alcohol, ether, and water, *p*-benzoquinone yields a pale yellowish-green solution. This, however, changes in sunlight to a greenish-brown, and subsequently to a deep red colour, in the case of both the alcoholic and aqueous solutions. The ethereal solution, on the other hand, remains unchanged for a very much longer period than the others, and the alcoholic is not so rapidly altered as the aqueous solution.

The Solution in Alcohol.—The absolute alcohol purchased was dried with a small quantity of freshly-ignited quicklime, filtered, and redistilled. On photographing the solutions, it was found that the absorption curve differed from that given in the *Brit. Assoc. Report,* in so far as the band with centre about $^1/\lambda$ 3400 does not appear strong in the alcoholic solution, but has the character of a considerable extension of the spectrum. The other two bands in the less and more refrangible rays, with centres about $^1/\lambda$ 2400 and $^1/\lambda$ 4100 respectively, are well shown.

The Aqueous Solution.—The absorption for the aqueous solution does not agree with the curve given in the Report already referred to; the band at $^1/\lambda$ 3400 does appear, but it is not at all as persistent as there represented.

This may be accounted for, first, by the more recent solution having been prepared while protected from the action of daylight, and secondly, by the much shorter period during which the solutions were exposed to the action of the rays of the spark when photographing the spectra. The other bands at $^1/\lambda$ 2400 and $^1/\lambda$ 4100 are strong.

The Ethereal Solution.—The band in the less refrangible rays is seen to be strong as far as $^1/\lambda$ 1500; no band appears at $^1/\lambda$ 3400, and the band in the more refrangible rays, $^1/\lambda$ 4100, is almost the same as in the alcoholic solution.

The measurements of the absorption bands cannot be read from Figs. 1 and 2 showing the curves of the respective solutions. The solution bands are compared with the vapour bands on p. 48, and also with the solution bands of quinol. The following table will greatly facilitate reference to the curves:

	Red.	Orange.		Yellow.	Green.		Blue.	Violet.
	A.	*B.*	*C.*	*D.*	*E.*	*F.*	*G.*	*H.*
$^1/\lambda$	1314	1455	1528	1696	1897	2056	2321	2519
λ	7604	6867	6562	5892	5269	4860	4307	3967

Ultra-violet solar lines.

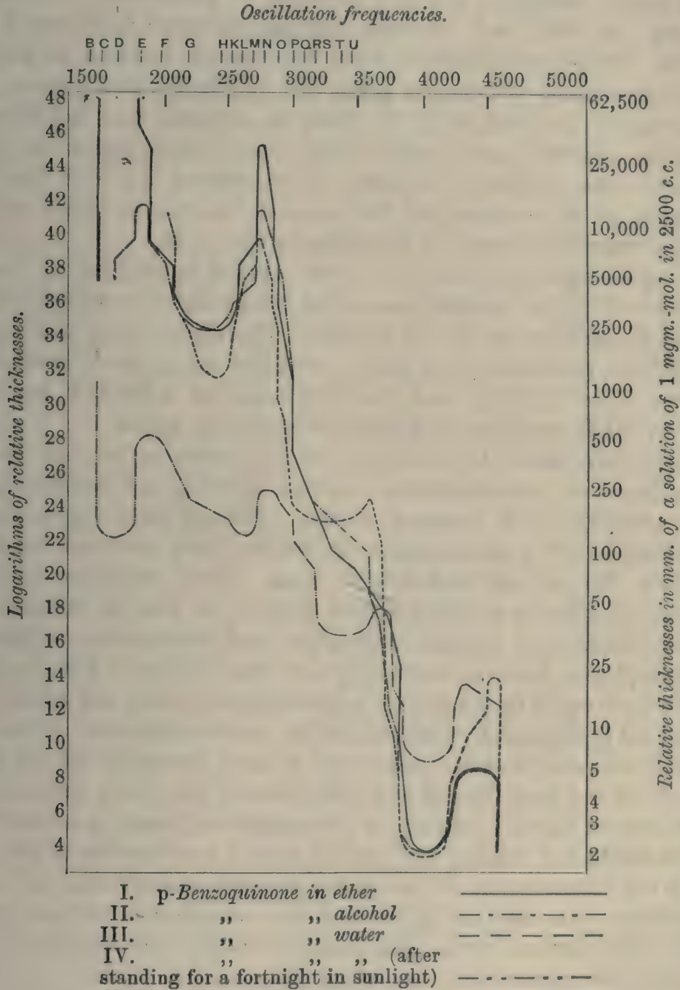
	K.	*L.*	*M.*	*N.*	*O.*	*P.*	*Q.*	*R.*	*S.*	*T.*	*U.*
$^1/\lambda$ ...	2542	2618	2683	2793	2907	2976	3044	3145	3225	3311	3396
λ ...	3933	3820	3727	3580	3440	3360	3285	3179	3100	3020	2947

A Comparison of the Solution Spectra.

The significance of the curves and the manner in which the properties of the solutions may be interpreted from them is of particular interest in the case of *p*-benzoquinone on account of the great range of the spectrum traversed, which is almost all that can be photographed through a quartz train and a solvent such as alcohol. Another feature of these spectra is the extraordinary extent of dilution to which the solution may be submitted before all the distinct bands become visible. Taking the curve of *p*-benzoquinone in ether (Fig. 1), the red rays as far as *C* and a little beyond are absorbed, then the rays are transmitted nearly as far as *E*, the line slopes towards a point half-way towards *F* at $^1/\lambda$ 1975, and beyond this all rays are absorbed; when viewed by transmitted light, therefore, the solution is of a bright reddish-golden colour. Where the curve passes through *O* and beyond *U*, there is an extension of the spectrum observed in all three solutions of *p*-benzoquinone. The rays between $^1/\lambda$ 4300 and $^1/\lambda$ 4650 are transmitted, but a band is shown between $^1/\lambda$ 3950 and $^1/\lambda$ 4300. Whereas the last band is measurable through no more than from 2 to 5 mm., the absorption in the green, blue, violet, and ultra-violet, or of all rays more refrangible than *E*, is at a proportional thickness of 62,500 mm. of a solution containing only 0·108 gram or 1 milligram-mol. in 2500 c.c., or a gram-molecular weight in 2500 litres.

The principal difference between the fresh solution of *p*-benzoquinone in water and in ether is a great transmission of the green rays to beyond *F* or $^1/\lambda$ 2100. The red rays are mixed therefore with more green, and the colour thus appears more distinctly greenish. Where the curve of the aqueous solution reaches a point at

FIG. 1.



Solution-spectra.

Q, a difference of a very significant character is seen in a sudden extension from $^1/\lambda$ 3040 to $^1/\lambda$ 3650. In other instances, this has been shown to be evidence of a tendency in the solution to change in constitution, and cause the formation of a substance with a band in the position of this extension. The curve of quinol in aqueous solution has its band in approximately this position (see Fig. 2).

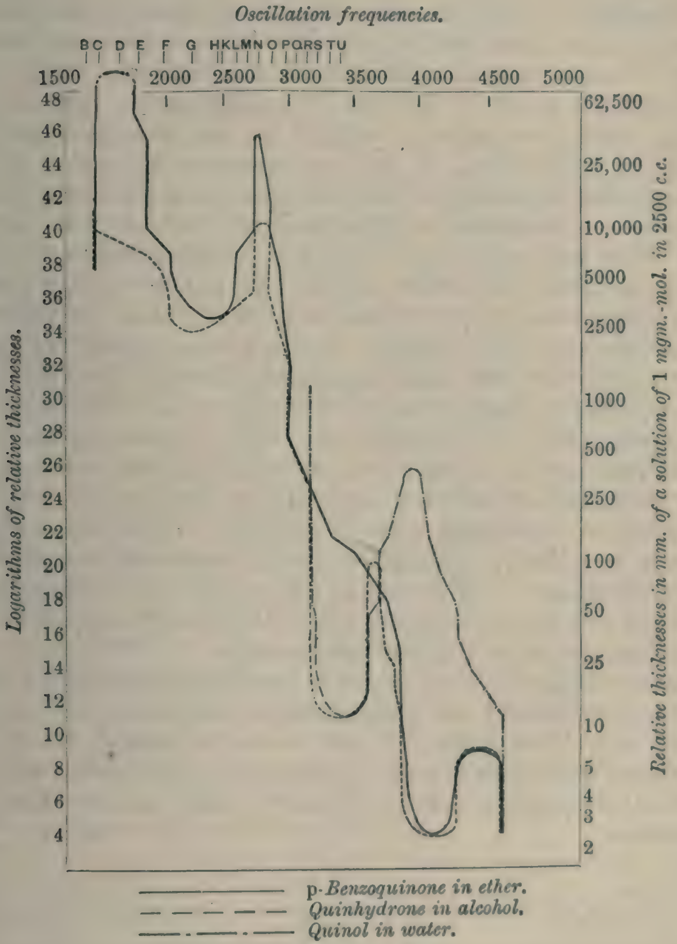
The curve of the solution of *p*-benzoquinone in alcohol differs widely from that in ether; it shows the solution to be much less transparent, and that no rays are transmitted less refrangible than *D*; at a somewhat greater thickness, the only visible rays transmitted lie near *E* between $^1/\lambda$ 1850 and $^1/\lambda$ 1975, the proportionate thickness being 10,000. This is very different from the ethereal solution at 62,500, where the orange, yellow, and green are still freely transmitted. In fact, near *C*, $^1/\lambda$ 1560, to *Q*, $^1/\lambda$ 3000, the ethereal and the aqueous solutions resemble each other more closely than either of them resembles the alcoholic solution. It is beyond $^1/\lambda$ 3000 that the extension of the spectrum of the aqueous solution suddenly occurs, which is the chief element of difference in the curve.

When the aqueous solution has been exposed to sunlight, the resulting curve is full of interest, because of the evidence it affords of the change in constitution of the solution. The band lying between *F* and *M* still remains, but is greatly modified, being much shallower; between *S*, or $^1/\lambda$ 3200, and $^1/\lambda$ 3650 there is a distinct, but very shallow, band, coincident in position with that of quinol.

The peculiarities in the absorption of the visible rays in the spectra of solutions of *p*-benzoquinone in ether, alcohol, and water call for some remarks. For instance, it was observed that the greenish-yellow colour of *p*-benzoquinone in ethereal and alcoholic solutions was not due to any well-defined band. Such solutions as were distinctly yellow or greenish-yellow showed no line of demarcation in the visible rays between absorption and transmission either on photographs or when controlled by eye observations. This was the meaning conveyed in a previous communication, when the colour was attributed to a general absorption in the visible spectrum. When the solution is yellow, this is caused by a greater absorption of the blue, green, and red rays than of the yellow, which are freely transmitted. In the brown aqueous solution of *p*-benzoquinone there is a quenching of the bright red, orange, and yellow, with a transmission of the red, and a full transmission of the green, but with absorption of the blue and violet. The solution is coloured by a mingling of red and green rays, which produce brown, but, notwithstanding the darkness of the colour, it was impossible to say where the spectrum terminated in the red. Bands which appear in the spectra of highly concentrated solutions, when they are due to the carbonyl group, have not such sharply-defined boundaries as those generally observed in benzenoid derivatives.

Recurring to the absorption spectra of the solutions of quinol and quinhydrone, also of *p*-benzoquinone in ether, alcohol, and water respectively, the chief point of difference between the latter appears to reside in the tendency of *p*-benzoquinone to undergo reduction to quinol, and consequently to form quinhydrone, being different in the three solvents. In ether, the band believed to be due to quinol at $^1/\lambda$ 3100 to 3600 does not appear at all; in alcohol the same band takes the form of an extension of the spectrum. This is the usual appearance when a substance is undergoing change, as has already been observed in some of the diureides and other tautomeric substances when the change has not become pronounced.

FIG. 2.



Solution-spectra.

In the aqueous solution, the band is definitely shown, but it rapidly disappears on dilution. The p-benzoquinone solutions exhibit a remarkable transparency for rays about $^1/\lambda$ 1750, namely, near D, and in the case of the ethereal solution these rays are still transmitted through 100 mm. of a solution containing 25 milligram-molecules in 100 c.c.

A comparison of the absorption curve of quinhydrone with those of p-benzoquinone and quinol (Fig. 2) shows at first sight what appears to be evidence that the union of the two molecules $C_6H_4O_2$ and $C_6H_4(OH)_2$ is not of a very firm or binding nature, for each part of the quinhydrone molecule exhibits its own absorption spectrum almost as completely as if the two substances composing it were photographed separately and the one photograph superposed on the other, or as if the action of the solvent had split the molecule into two. Thus the curve shows the band of p-benzoquinone with centre at $^1/\lambda$ 2400, the quinol band at $^1/\lambda$ 3400, and the further p-benzoquinone band at $^1/\lambda$ 4100. Moreover, these bands are shown at almost the same concentrations as for p-benzoquinone and quinol respectively, but with these significant differences, that the bands are shifted very slightly towards the red end of the spectrum, and the two bands in the less refrangible rays begin to appear at less thicknesses than they do in the spectra of p-benzoquinone and quinol, in fact, in the coloured rays the absorption is much altered. The band in the more refrangible rays is unaffected, because at the great dilution at which it appears, the general absorption has ceased to affect the spectrum. The band in the quinhydrone spectrum, corresponding with the p-benzoquinone band at $^1/\lambda$ 2400, is rather broader than it appears to be in pure p-benzoquinone.

By the comparison of the spectra of the ethereal solution of p-benzoquinone with those of the same substance in alcoholic solutions, it is clearly proved that alcohol is not a suitable solvent, because the p-benzoquinone tends towards reduction to quinol, even when no measurable quantity can be found to have actually undergone reduction.

Proof of the Reduction of p-*Benzoquinone in Aqueous Solutions.*

A solution of p-benzoquinone in water, exposed to sunlight during twenty-four hours, still contained p-benzoquinone. On boiling and evaporating to dryness, crystals resembling quinol were seen with the microscope lying amidst the blackish-brown, amorphous residue. On the addition of ferric chloride and boiling, a pronounced odour of p-benzoquinone was observed. Further proofs were obtained when operating on a large quantity of p-benzoquinone boiled with water.

This evidence confirms the view that the *p*-benzoquinone undergoes reduction, and that the second band in the absorption curve is the band corresponding with quinol. Furthermore, that when the band is pronounced, it is due either to quinol or to quinhydrone in the solution. The occurrence of quinol in the brown substance produced by warming a *p*-benzoquinone solution with sodium acetate was observed by Hesse (*Annalen*, 1883, **220**, 365), who extracted it by dissolving it in ether. The formula for quinhydrone is

$$HO\cdot C_6H_4\cdot O\cdot O\cdot C_6H_4\cdot OH.$$

The Occurrence of a Reversible Reaction, $C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + H_2$.

When comparing the absorption spectra of *p*-benzoquinone in a state of vapour with those of the solutions of *p*-benzoquinone in ether, it was found that a series of vapour bands lying between λλ 3051 and 2839 had no corresponding solution bands. The solution band of quinol, extending from λ 3128 to λ 2573, was found, however, just to cover the series, and accordingly the vapour spectrum of quinol was photographed to ascertain whether quinol vapour actually exhibits a band at λ 2900, as, if so, this would account for its occurrence in the *p*-benzoquinone vapour spectrum by a simple chemical change.

(I). Quinol (0·0081 gram) was heated in the metal tube, and its spectrum photographed at different temperatures. After the first series of photographs had been taken, it was observed that white light entering the tube became distinctly yellow, owing to the colour of the contained vapour, and on cooling, this was accounted for by finding that an appreciable quantity of *p*-benzoquinone separated out in the crystalline form. The contents of the tube in this and other similar experiments had the pungent odour of *p*-benzoquinone.

(II). Solid quinol was then vaporised in an atmosphere of dry carbon dioxide, this being a neutral gas, and also in hydrogen, as it was thought that any chemical interaction in this case would be one of reduction.

In both cases, *p*-benzoquinone was formed, but the quantity formed in the hydrogen atmosphere was small.

(III). As a more suitable reducing atmosphere, hydrogen mixed with alcohol vapour was next employed, when it was found that under these conditions no *p*-benzoquinone was formed. These observations were repeated, and the spectrum of pure quinol obtained in this manner shows a powerful band of absorption extending from λ 3080 to λ 2875, corresponding, therefore, with the solution band lying between λ 3128 and λ 2573.

The following tabulated statement enables one to compare the spectra of *p*-benzoquinone and quinol in a state of vapour with *p*-benzoquinone in solution.

Measurements in Wave-lengths and Oscillation Frequencies of the Bands in the p-*Benzoquinone Solution Spectra which Correspond with Groups of Bands in its Vapour Spectra and likewise with those in the Vapour Spectra of Quinol:*

p-Benzoquinone.				Quinol.		
Vapour bands.		Aqueous solution. Solution bands.		Vapour bands.		
λ.	1/λ.	λ.	1/λ.			
4383	22815 s.	5086	19662			
21	23142					
4270	23419					
44	562					
161	24032 s.					
015	906					
3789	26392 f.	3612	27685			
49	673			λ.	1/λ.	
3051·5	32770	3128	31969	3080	32467	
31	992					
22	33090 f.					
2991	433					
59	33795 f.					
54	852					At 170°
2888	34626 f.					
79	734					
73·5	34800 f.					
62·5	950					
53	35050 f.					
39·5	35217	2573	38865	2575	38834	
2527·5	39564	2540	39370	2538	39401	
2523	39635					
21	666					
05·5	912					
01	934					
2499·5	40008					
96	64					
56	716					
49	833					
38	41017					
29·5	160					
22·5	279					
19	339					
16	390					
13	442					At 100°
08	528					
06	562					
2399·5	674					
91·5	814					
80·5	42007					
76	42087					
75	105					
70	194					
59	390					
54·5	470					
54	480					
50	553					
47·5	597					
43·5	670	2313	43233	2430	41152	
25 bands.		3 bands.		2 bands. Rays more refrangible than λ 2430, and at 100° are transmitted. At higher temperatures, a general absorption obscures the rays.		

Thus it has been proved that *p*-benzoquinone has a tendency to change into quinol, and quinol unquestionably is converted into *p*-benzoquinone until there is an equilibrium between the two at temperatures about 150°, in the sense of the following equation:

$$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + H_2.$$

In order to make sure that the quinol examined should be quite free from *p*-benzoquinone, a strong aqueous solution was prepared, and sulphur dioxide was passed into it until the yellow, crystalline compound, $(C_6H_6O_2)_3,(SO_2)_2$, separated out; this was collected, and boiled with distilled water to expel sulphur dioxide from the solution; on cooling, quinol separated in beautiful, colourless needles. This sample was used for the first vapour spectra, which were photographed from quinol vaporised in air, and a further sample was recrystallised from water containing sulphur dioxide. From the method of preparation and the care exercised, no *p*-benzoquinone could possibly have been present as an impurity in the crystallised quinol.

Examination of the Substance obtained from the Aqueous Solution of p-*Benzoquinone.*—An aqueous solution of 0·44 gram or 5 milligram-mols. of *p*-benzoquinone in 100 c.c. was kept for about a month. A brown solution and a precipitate of similar colour gradually formed. The solution appeared to be muddy, and from the fact that no filtering process could render it clear, it was evidently of a colloidal character. The dark brown precipitate is soluble in hot water, but again the liquid is not clear, and, on cooling, much of the solid separates as before. The substance thus produced dissolves in sodium hydroxide solution, yielding a clear reddish-brown liquid. It dissolves in alcohol, also yielding a similar solution, which, when evaporated to dryness, leaves a dark brown, amorphous residue devoid of crystalline character. This residue, when extracted with ether, partly dissolves, forming a red solution, which yields, on evaporation, an amorphous, reddish-brown residue. The reddish-brown powder, when washed with water on a filter, forms a dark red solution, which, on adding 2*N*-hydrochloric or sulphuric acid, deposits a reddish-brown precipitate easily soluble in a solution of sodium hydroxide.

It appears to be identical with the original compound deposited from *p*-benzoquinone solutions. When examined under the microscope, the powder is seen to be of a coarsely flocculent nature, showing no trace of crystalline structure even after some days. On mixing the moistened substance with chloroform, a treatment which in similar cases admits of the presence of two substances being discovered by the microscope,* there was no trace of another compound to be seen. The substance was not a mixture, but a homogeneous, flocculent, colloidal colouring matter. Neither sulphur dioxide nor carbon dioxide when passed into solutions of the brown powder caused any apparent change. It dissolves in nitric acid to a clear yellow liquid, which becomes yellowish-brown on addition of sodium hydroxide. With a mixture of nitric and hydrochloric acids, a yellow, crystalline precipitate is formed and the solution becomes green.

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* I have frequently employed, with advantage, this method of disentangling crystalloid from amorphous substances, and of separating crystalloids of different

The residue from the evaporation of an ethereal solution is partly soluble in water, and, on heating it with a solution of ferric chloride, a strong reddish-brown coloration is produced. The crystalline substance resembles tetrachloro-*p*-benzoquinone, and the ferric chloride reaction suggests a hydroxyl (phenolic ?) derivative, as also does the solubility in sodium hydroxide, with precipitation therefrom by neutralisation with an acid.

The Decomposition Products of p-*Benzoquinone.*

Several grams of *p*-benzoquinone were boiled with 3 litres of water in a flask with a reflux condenser attached, for a period of twenty hours. A considerable quantity of the brown substance separated, which was filtered off, washed four times with water on a pressure filter, and then dried.

The filtrate was boiled as long as there was any further precipitation, but only a small additional quantity of substance was obtained. After the second filtration the liquid gave no odour of *p*-benzoquinone when boiled, but after the addition of ferric chloride solution, it smelt strongly of that substance. The liquid very rapidly reduced Fehling's solution. These reactions, in connexion with those previously described, demonstrate the production of quinol. Since by boiling the filtrate there was no evidence obtained of the presence of *p*-benzoquinone, there could have been no quinhydrone in the liquid. But as quinol is one of the products from *p*-benzoquinone, the original substance, at some intermediate stage, quinhydrone must have been formed, therefore when, as in this case, the reaction has been carried to completion, the last molecule of quinhydrone must have been reduced to quinol.

The brown precipitate, when purified, did not reduce Fehling's solution, nor was it oxidised by ferric chloride into *p*-benzoquinone.

On endeavouring to dissolve the brown powder in alcohol in order to make a molecular-weight determination, it was found to be only partly soluble. The residue was insoluble in ether, but readily

characters as, for example, in proving that, in addition to the chief product murexide, a mixture of two different colourless substances resulted from the interaction of alcoholic ammonia and alloxan (W. N. Hartley, Trans., 1905, **87**, 1807).

soluble in sodium hydroxide solution. It thus appears that this colloidal substance had altered in solubility on keeping, probably by coagulation. When heated in a glass tube, the dried powder charred, and an odour resembling that of phenol was perceived, whilst reddish-brown needles condensed on the cool sides of the tube. Solution of these in water gave a precipitate with bromine water, which was apparently tribromophenol.

The Composition of the Brown Substance.—The colloidal nature of the compound rendered it difficult to purify. Out of four combustion analyses, two yielded percentages of carbon and hydrogen corresponding satisfactorily with the formula $C_{12}H_8O_5$:

Found: (1) $C = 62{\cdot}08$; $H = 3{\cdot}46$. (2) $C = 62{\cdot}05$; $H = 3{\cdot}44$.
$C_{12}H_8O_5$ requires $C = 62{\cdot}06$; $H = 3{\cdot}44$ per cent.

The other two agreed more nearly with $C_{12}H_7O_5$:

Found: (1) $C = 62{\cdot}56$; $H = 3{\cdot}08$. (2) $C = 62{\cdot}31$; $H = 2{\cdot}94$.
$C_{12}H_7O_5$ requires $C = 62{\cdot}33$; $H = 3{\cdot}03$ per cent.

The formula $C_{12}H_8O_5$ is probably the more correct.

Conclusions.

1. The absorption spectrum of *p*-benzoquinone has been obtained by vaporising the dry crystals in air at temperatures varying between 17° and 147°.

2. The only suitable solvent in which the true spectra of *p*-benzoquinone at all concentrations can be observed is pure dry ether, and from photographs of the ethereal solutions the molecular vibration curve has been drawn.

3. Under the action of sunlight and ultra-violet rays, an interaction between the solvent alcohol and the solute *p*-benzoquinone occurs, which leads to the reduction of *p*-benzoquinone to quinol; its effect on the visible spectrum causes an absorption between *C* and a point approaching *E*, with consequent change in the colour of the solution.

4. Water is a solvent less suitable than alcohol, inasmuch as the chemical interaction takes place more rapidly and readily, yielding a strongly-coloured brown substance along with quinol.

5. Evidence of the chemical reactions induced by the solvents alcohol and water was first afforded by the molecular vibration curves, and from similar evidence it has been concluded that quinhydrone does not undergo dissociation when dissolved in alcohol, for, although it shows absorption bands corresponding with those of both its constituent substances, the bands have undergone considerable modifications.

6. A reversible reaction occurs according to the following equation: $C_6H_6O_2$ $C_6H_4O_2 + H_2$, when *p*-benzoquinone vapour is heated in air at 147° at atmospheric pressure. When heated in hydrogen, the quantity of *p*-benzoquinone produced is diminished. Its formation is completely prevented by the presence of alcohol vapour.

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VII.—*The Constitution of para-Benzoquinone.*

By WALTER NOEL HARTLEY.

IN 1905 it was shown that the formula for benzene as proposed by Kekulé might be reconciled with those of Armstrong and von Baeyer (Trans., 1905, **87**, 1822). It was, furthermore, explained how the chemical properties of *p*-benzoquinone could be accounted for by the double ketonic formula occurring once as a phase in the vibrations within the molecule, with the peroxide formula occurring as another phase twice, so that in successive periods two different chemical reactions would be possible with the same molecule, conferring on it a dual character. From the evidence obtained during the investigation of *p*-benzoquinone, quinol, and quinhydrone in a state of vapour and in solution, and of vapour spectra and solution spectra of benzene and its homologues (*Phil. Trans.*, 1908, *A*, **208**, 475), it now appears certain that neither *p*-benzoquinone nor quinol are compounds with a fixed and settled constitution in the strict sense of their usual symbolic representations, or the interpretations of them.

In the spectra of *p*-benzoquinone in a state of vapour and dissolved in water, there are two very characteristic absorption bands, one at each end of the spectrum; that in the visible region is due to the ketonic complexes, the second is to be ascribed to the benzenoid nucleus. In solutions in ether and alcohol the benzenoid band is not evident at first sight, because, from its diffuse character, it is difficult to ascertain its termination, but it does not extend to λ 2194. Had this absorption been observed merely in solution spectra, its bearings on the question of the formula and constitution of *p*-benzoquinone would have much less importance than if it were identified with benzene by an examination of the vapour spectra.

It is necessary to point out that in both the vapour spectra and solution spectra there are two kinds of absorption which are sharply defined and may be differentiated, namely, the general absorption caused by the translatory kinetic energy of the molecules, and selective absorption due to vibrations of the atoms or atom complexes within the molecule. These deductions are based on evidence afforded by observations on the effects of temperature and pressure on the vapour spectra of benzene (*loc. cit.*).

It has been proved experimentally that increase of mass, of density, and of temperature operate in the same manner on the rays entering a column of benzene vapour; in the first place, the general absorption is increased by an extension towards the visible rays, and it is also intensified; in the second place, the bands of absorption broaden, become diffuse, and coalesce. As the bands attributed to the internal vibrations of the parts of the molecule in different isomeric hydrocarbons become diffuse and coalesce, partaking of the character of the general absorption, and as this is not confined to one part of the spectrum, namely, to the less refrangible of the transmitted rays, but is a selective absorption, it cannot be due to simply a loading of the molecule; if it were, then it would be impossible to distinguish between the three isomeric xylenes so as to identify them by a simple inspection of their absorption spectra, or even to distinguish them from ethylbenzene.

It may be conceived to be due, in part, to an irregularity in the motions of the molecules, such as would arise from encounters between unsymmetrically shaped bodies; or if of symmetrical form, such as vortex rings or spheres, the rings or spheres being not throughout of uniform density; in other words, the distribution of mass within the molecule being different for each isomeride.

The same effect on the spectrum as that due to a want of uniformity in the distribution of the mass of the parts within the molecule could be brought about by periodic contractions and expansions occurring within it.

It is conceivable that it might be caused by a transference of a part of the intramolecular energy to the kinetic energy of the molecule, the intramolecular vibrations being actuated by the radiant energy of the spark.

If the variations in the distribution of the masses within the molecule, which have been likened to contractions and expansions, do not result in any loss of energy, there must be a transference of chemical energy from point to point in the molecule, and each contraction must lead to augmented chemical activity.

To make this easily understood, it is necessary to point out once more the endothermic character of benzene, and compare it with that of another endothermic molecule, namely, ozone (Trans., 1893, **63**, 243).

The reaction $3O_2 = 2O_3$, as implied by the formulæ, is accompanied by increased density and by contraction in volume, with a greater chemical activity. At the same time the stability of the molecule is lessened, and its absorption of both the ultra-violet and the visible rays is enormously increased, the spectrum in the ultra-violet being characterised by a broad and powerful band.

The vibratory motions within the molecule of benzene may be correlative with the transference of chemical energy from point to point in the molecule, that is to say, successive pairs of carbon atoms.

Compounds are either endothermic or exothermic according as they gain or lose energy in their formation, and as we cannot dissociate matter from energy, a compound in solution in the state of vapour or liquid may appear to be essentially different in constitution from its condition as a solid, although this may really be only a question of degree. In fact, we know now how frequently substances when dissolved undergo changes in properties, which are explained by hydrolysis, ionisation, and tautomerism or desmotropy. The diverse chemical reactions exhibited cannot be represented by any single structural formula for each such substance; and the large number of organic compounds to which on rational grounds more than one formula may be assigned, for instance, all dyes and coloured substances for which various quinonoid formulæ have been proposed, appear to have one physical characteristic in common, in that they are all endothermic compounds, or in cases where a series of compounds may on the whole be exothermic, they will be found to contain complexes of an endothermic character, and these are the most chemically active parts of the molecule.

Such substances are benzenoid derivatives, oximino-ketone rings, diureides, and certain open-chain compounds with keto-ethylenic linkings, first examined by Wallach (*Nachr. K. Ges. Wiss. Göttingen*, 1896, 1), and later by Baly and Desch (Trans., 1904, **85**, 1029).

In a change of this nature, where a complex which is exothermic becomes one which is endothermic, it follows that there must be a transference of the energy with which the latter is endowed to another atom or complex which has an exothermic value, and so on with successive atoms and complexes continuously. The effect of this transference of energy would be to confer on the six carbon atoms of benzene something like equality in so far as it would be impossible to associate the energy (free energy according to the expression of v. Helmholtz) with any individual carbon atoms, and hence we arrive at a constitution for the benzene molecule the special properties of which are intended to be represented by the centric formula.

Supposing that a substance is in such a condition that it is neither enolic nor ketonic, it is evident that the molecular vibration curve will afford no conspicuous evidence of one or the other isomeride, but it might be expected to exhibit a feeble character common to both of them or tending towards one of them. Let us consider how this would appear on the molecular vibration curve when a well-defined absorption band is characteristic of one of the forms which a substance might assume; in the first place, the band, if it appear at all, would be ill-defined, and it would be a shallow band easily extinguished by dilution. It would appear with larger concentrations than those of either the enolic or ketonic form. Let us then suppose that we have a means of converting it into an enolic compound by the addition of some suitable reagent, then the enolic form becomes pronounced in the character of the curve, the boundary of the band is sharper, the band itself is more intense, and it extends through a greater range of concentrations. This is exactly what we find with certain oximino-ketone compounds and diureides (Hartley, Trans., 1905, **87**, 1791), also with phthalic anhydride (Hartley and Hedley, Trans., 1907, **91**, 314), in presence of water.

It is striking in the case of violuric acid and its sodium salt, in uric acid and lithium urate, and in the series of reactions involved in the conversion of alloxan into murexide (*Trans. Sixth International Congress of Applied Chemistry*, Rome, 1907, **3**, 397; Trans., 1905, **87**, 1791, 1798).*

Let us, however, suppose a compound to be composed of two parts, one of which is ketonic and the other enolic, both of a very pronounced type, then by dissociation in solution the spectrum curve would show the spectra belonging to each molecule as if the two were mixed, or the curve of the one were superposed on the other, and if the characteristic bands were far apart, there would be no interference of one with the other.

In the event of there being no dissociation, we should still expect to find the ketonic and enolic bands in the curve, but modified to some extent in neither being so pronounced as in the original constituent substances.

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* Since the above passage was written, the British Association Reports on *Dynamic Isomerism*, 1907 and 1908, have been perused, wherein a most interesting account is given of the action of a third substance in determining isomeric changes. In a neutral solvent it appears that the change is not spontaneous, but is determined by the presence of minute traces of alkaline impurities. Such an instance has been described by me in the case of violuric acid (Trans., 1905, **87**, 1798). T. M. Lowry expresses the opinion that it is very doubtful whether the process of "band shifting" or desmotropy described by Stewart and Baly as isorropesis (Trans., 1906, **89**, 498) could occur in pure neutral solvents in the absence of a catalytic agent, as probably water and even alcohol are effective in causing such changes, and Baly has suggested some change by the action of water on *p*-benzoquinone. As already shown in the preceding paper, it undergoes reduction in ultra-violet light. When experimenting on vapours the case is different, and it is only by intramolecular vibrations that the numerous bands observed in the absorption spectra of the substances can be accounted for, but the presence of another gas or vapour will determine the nature of the change, as in the case of *p*-benzoquinone and quinol.

Now a substance fulfilling these latter conditions is quinhydrone. An aqueous solution, freshly prepared from *p*-benzoquinone, shows two bands, one at great concentration at the red end and another at very small concentrations in the ultra-violet, but there is an intermediate point between the two, almost coincident with a band of quinol, although somewhat more extended towards the red, where there occurs a marked extension of the spectrum, like a very shallow band, which is evidence of a tendency to form a band at this position. At the least refrangible end, red and yellow rays are transmitted (see curve p. 45).

Let us now take quinol; the characteristic band extends through a considerable range of concentrations, but it is confined strictly within definite bounds.

With quinhydrone in aqueous solution, we have all three bands, the two of quinone and the one of quinol, a combination of the two curves, with some modifications in the bands.

Thus the band in the blue is less intense, and it is widened out towards the red so as to absorb the intermediate rays much more strongly, and as far as *C* they are absorbed, the less refrangible rays being transmitted. The result is that, at similar concentrations, quinhydrone is much more strongly coloured than *p*-benzoquinone, and from observations of the curve its colour is evidently green. The continuation of the curve then follows that of *p*-benzoquinone until it approaches the position of the quinol band, when it undergoes a slight modification, and the band of quinol is well developed, but it becomes somewhat narrower and more intense, and the second well-defined band of quinone, far in the ultra-violet, is evident. These are all the essential elements of the two curves, but with some considerable modifications in the visible spectrum which show that the molecule has not undergone dissociation.

If we turn to the *p*-benzoquinone aqueous solution, it is seen that there is an extension of the spectrum in or about the position of the quinol band, analogous to that observed in phthalic anhydride, but in this case it is indicative of a tendency to form quinol. In the spectra of the old solution, the band is slightly more pronounced, and we have evidence in this case that quinol is produced, because it has been actually found in the solution.

On examining the curve for the alcoholic solution of *p*-benzoquinone, it will be seen that, although there is no band similar to that of quinol, there is an extension of the spectrum, which indicates a tendency to form a band at this point, that is to say, there is a tendency to form quinol. With the ethereal solution of *p*-benzoquinone, this has practically disappeared. All three solutions indicate the benzenoid band (see Fig. 1, p. 43).

We now arrive at the discussion of the constitution of the *p*-benzoquinone molecule.

It has already been shown that it may be simply a double ketone consisting of two chromophoric groups, $\cdot C{:}O\cdot C{:}C\cdot$, common to certain open-chain compounds, and, therefore, not necessarily constituted on a benzene ring; but against this view, it may be pointed out that the spectrum would show only a keto-enolic band, of particular intensity or width, it is true, but without the character of those bands which are derived from benzenoid compounds.

It must be admitted that the dynamic constitution of benzene is now founded upon such facts that it has passed the stage of a mere hypothesis, and as *p*-benzoquinone in a state of vapour assumes the potential properties of a double ketone, a peroxide, a dihydroxybenzene, and benzene itself, according as we correlate the different bands in its absorption spectra with its chemical properties under the action of light, and in presence of hydrogen, or of oxygen, this can only arise from the vibratory motion of the atoms within the molecule.

Having arrived at this decision, it remains for me to present the final proof of *p*-benzoquinone being constituted on the benzene nucleus. This would be attained if the numerous bands in the vapour spectrum of *p*-benzoquinone could be identified with similar bands in the spectrum of benzene. Accordingly, the bands already tabulated in the foregoing paper were compared with the corresponding bands in the spectrum of benzene taken from table VII, p. 506, in the *Phil. Trans.* (*loc. cit.*). It will be seen that the fifteen bands in the *p*-benzoquinone spectrum are easily identified with similar bands or pairs of bands in the spectrum of benzene.

Furthermore, a careful examination of the bands comprising this third group shows that, with the exception of λ 2527 (see p. 516, *loc. cit.*), there are no corresponding bands in the vapour spectra of toluene, ethylbenzene, and the three xylenes; they must therefore be attributed to vibrations within the *p*-benzoquinone molecule, that is to say, within the benzene nucleus, and not to the translatory kinetic energy of the molecules (see p. 521, *loc. cit.*).

Comparison of the wave-lengths of the bands composing the vapour spectra of *p*-benzoquinone and benzene respectively, which correspond with the absorption in the most refrangible rays observed in their solution spectra.

Abbreviations, *s*, strong; *f*, fine; *s n*, strong narrow; *v s*, very strong; *v f*; very fine.

p-Benzoquinone vapour bands. λ.	Benzene vapour bands. λ.
2527·5	2527 *s.*
23	22 *s.*
21	21 *f.*
05·5	06 *s.*
01	
2499·5	2499 *s.*
96	96 *s.*
56	54 *s.*
49	48 *f.*
38	39 *s.*
29·5	30 *s.*
22·5	23 *s n.*, also 21 *s.*
19	19·5 *s.*
16	15·5 *v s.*
13	13
2408	2409 *s.*
06	07 *v f.*
2399·5	00 *s.*
91·5	
80·5	2379 *f.*
76	also 77 *f.*
75	75 *s.*
70	also 72 *s.*
59	58 *f.*
54·5	
54	52 *v f.*
50	
47·5	49 *v f.*
43·5	44 *s.*

To account for the great difference between the spectrum of *p*-benzoquinone and that of other benzene derivatives, it is necessary to contrast the effect on the absorption spectra consequent on the replacement of hydrogen in benzene by other hydrocarbons (the coalescence of the narrow bands, etc.) with the effect of the ketone complex in substances other than benzene, such as oximino-ketones, diureides, and camphor. The presence of the carbonyl group is characterised by a broad absorption band, which appears only in comparatively large concentrations, and soon disappears after dilution, but with two such bands in the molecule the absorption is naturally intensified. By the combined effect of two such characteristic absorption phenomena in the one molecule, we arrive at the curve for *p*-benzoquinone.

I may add that the further investigation of the reversible reaction mentioned in the previous communication is being now carried out in order to ascertain the conditions of equilibrium.

Conclusions.—Taking into account the previous work on *p*-benzoquinone and its derivatives, *p*-benzoquinone-chloroimide, -dichloroimide, *p*-benzoquinone-oxime and -dioxime, with its chemical reactions as a powerful oxidising substance under the influence of light, and the more recent experiments on the vapour and solution spectra, of *p*-benzoquinone, quinol, and quinhydrone, there appears to be now no doubt that *p*-benzoquinone is a benzene derivative.

Furthermore, that it is possessed of a dual character in the sense that the function of the molecule can be either that of a double ketone or of a peroxide, according to circumstances.

It is evident that a similarly dual character belongs to many other benzenoid and keto-ethylenic compounds, of which tautomerism, dynamic isomerism, fluorescence, and colour are particular manifestations.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

VIII.—*The Electrical Conductivity of Phosphoric Acid.*

By HARRY EDWARD WILLIAM PHILLIPS, M.A., B.Sc.

UNTIL the recent work of Jones, Getman, and Bassett, the only information as to the conductivity of ortho-phosphoric acid was to be found in the few determinations of Arrhenius and the first work of Kohlrausch, who made conductivity measurements of nine strengths of acid at 18°.

In these measurements, no particulars are given as to the method of preparing the acid, except that Jones and Getman state (*Zeitsch. physikal. Chem.*, 1904, **46**, 244) that they obtained it in a "well-crystallised condition" and that the lower concentrations were obtained from the "standardised mother-solution by dilution."

In the present work, the following was the method used to prepare the pure acid. Phosphorus trichloride twice redistilled was mixed very slowly with specially purified water, the flat porcelain dish in which the addition was made being floated on cold water during the operation. It was found that, if the addition was made too rapidly, a discoloration was produced, which at the end of the preparation was seen to be due to a fine powder suspended in the liquid. The phosphorous acid was then heated until it gave no precipitate with silver nitrate. It was then oxidised by cautious addition of pure dilute nitric acid, when an active effervescence ensued. Nitric acid was eventually added in slight excess, and evaporation continued until all this was expelled.

The acid thus prepared was a transparent, colourless substance. Analysis showed the absence of iron, arsenic, lead, cadmium, sulphuric, nitric and hydrochloric acids. Gravimetric analysis showed concordance with the percentage indicated by its specific gravity. The 100 per cent. acid did not crystallise, even on cooling to 0°, but one specimen of 43·26 per cent., after some time, began to crystallise, and on adding a portion of this solution containing crystals to the other high percentage samples, crystals were obtained. These crystals were small and apparently soft, almost gelatinous. They disappeared on gentle heating, and on no other occasion were they formed spontaneously. The 100 per cent. acid does not affect litmus paper, and is without action on sodium carbonate.

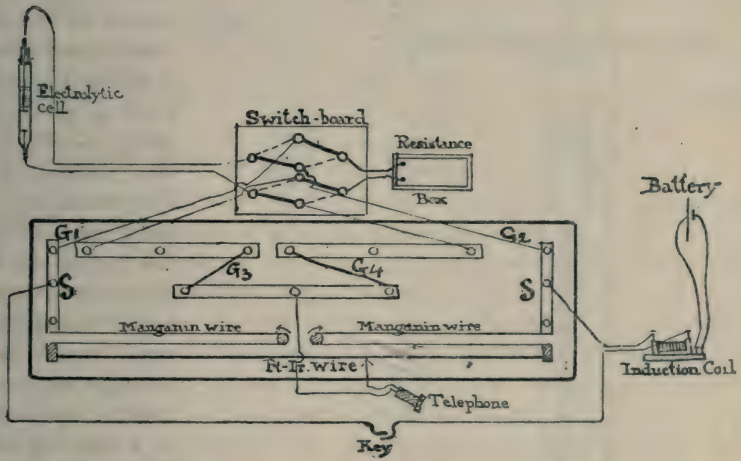
Analysis.—To analyse the acid, the lead oxide gravimetric method used by Watts (*Chem. News*, 1865, **12**, 160) in his density determinations was adopted. Pure lead oxide was prepared from lead nitrate thrice recrystallised, and when thus prepared and protected from organic matter, it could safely be heated in a platinum crucible. The operation consisted in merely adding to a weighed quantity of oxide a weighed quantity of the phosphoric acid solution, and heating until all the water was expelled. It was found difficult at first to obtain successive concordant weighings, but this was found to be due to the method of weighing, the platinum crucible being placed on the bare pan. Two pairs of light blown glass bottles with ground hollow stoppers and without necks were made for the platinum crucibles, so as just to accommodate them, one of each pair being used as a counterpoise, and the other containing the crucible. By this means the glass surface presented on both pans of the balance was equal, and the weighings became concordant.

The pyknometer employed was the bottle-shape, with thermometer stopper and side capillary tube with cap. Sprengel's shape was tried, but the viscosity of the higher strengths of the phosphoric acid made it impracticable in use. To make a specific gravity determination, the acid was run out of the cell into the bottle, which was then transferred to a thermostat with a revolving vane.

The Water.—The water used throughout the experiments was distilled by a modification, devised by Manley, of the apparatus described by Jones andMackay (*Zeitsch. physikal. Chem.*, 1897, **22**, 237). Ordinary tap-water is boiled in a conical copper flask, and the steam passed through a second flask, which contains acid permanganate. This flask is also heated by a small flame. The steam then passes into a third flask, which contains acid permanganate, and on leaving this, the steam is condensed in a block-tin condenser. There is also a trap which prevents regurgitation.

The Bridge.—The bridge employed was made expressly by the author for the work. Profiting by the experience of Veley and Manley (*Phil. Trans.*, 1898, **191**, *A*, 365) in their measurements of the conductivity of nitric acid, a bridge was made in some respects similar to the one used by them, but instead of the bridge wire being two metres in length, only half a metre of specially drawn platino-iridium wire is used. The whole metre did not seem necessary, as the resistances are always arranged so as to bring the slider contact near the middle of the bridge, and additional delicacy is secured by adding to the main wire at each end a thin wire of manganin alloy mounted parallel to the main wire, which, on each side starting from the same brass clamp as the main wire, is continued to the middle of the bridge; there it makes a turn on a fixed ebonite drum, and returns to a brass clamp similar to the one used for the platino-iridium wire, and mounted on the same slab of ebonite, but air-insulated from it. This is connected with the first copper strap at each end by a short piece of copper wire. The bridge-end resistance is therefore due to the combined effects of the contacts of the brass clamps, the brass clamps themselves, the thin manganin wires and their contacts, together with the short pieces of connecting wires to the first copper straps. This

FIG. 1.



has the result of making the effective wire-length greater for the relation:

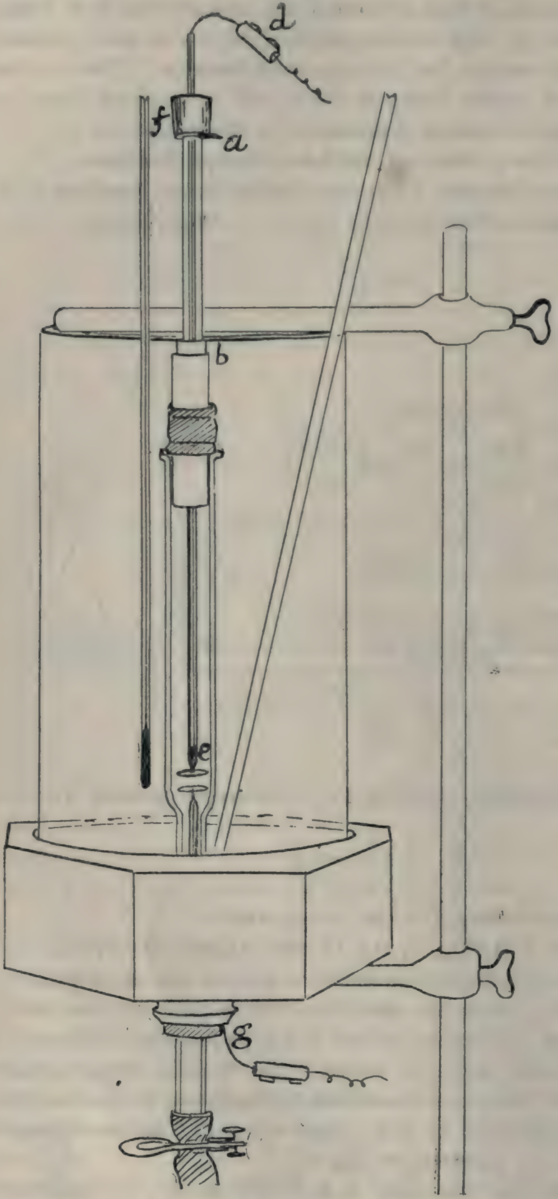
$$\frac{P}{Q}=\frac{1+(x_1-x_2)}{1-(x_1-x_2)},$$

where 1 is the effective length of the bridge wire.

The copper straps *S*, *S* (Fig. 1) are 12 mm. square in section, and are supported by being set at each end in a groove cut in a plate of ebonite 12 mm. thick, set on its side, this ebonite plate in turn being supported at each of its ends by slotted boxwood supports. Pieces of waxed paper just under each end prevent the ebonite from actually touching the board. Extremely satisfactory insulation is thus secured. Binding screws are soldered to the copper straps. The arrangement of these can be seen by referring to Fig. 1.

The slider and tapper combined is a simple rocker. Underneath two parallel lengths of brass tube, which are soldered to the heart-shaped end pieces, are two boxwood cones, also fastened to the end pieces with a wide slot in them, and these slots enable the slider to be drawn by the cord passing round the hand wheel at one end, along the plain glass tube fixed to the wooden base and parallel to the half metre scale. An ebonite arm carrying a brass binding screw, on to the underside of which is soldered a small piece of platinum wire, constitutes the tapping arrangement, and a small cord brings the tapper on to the wire by moving it through the very small arc through which it "rocks," by means of a lever at one end of the cord which also serves to keep the contact. When this cord is released, the weight of the slider "rocks" it back, and contact is broken, whilst the projecting brass piece then lies flat on the scale. This brass flap is pierced by a small mica window, which has a line scratched across its centre underneath,

FIG. 2.



so that through the hole the position of the slider on the scale can be easily read from the position of the scratched line in relation to the lines of the scale. The thin wire from the binding screw of the slider is connected with the middle of the bridge, and in this circuit the telephone is placed. The platino-iridium wire was carefully calibrated and found to be uniform, and to have a mean resistance of 0·0001455 ohm per mm.

The total resistance of the main wire, the manganin wire, and all connexions was calculated by Carey Foster's method, and found to be 0·5546 ohm. This, in terms of the platinum-iridium wire, made an effective length of $\frac{0{\cdot}5546}{0{\cdot}0001455} = 3812$ mm., so that the bridge was equivalent in delicacy to one of 3·8 metres in length, without the difficulties attending the stretching of such a length of wire.

This can best be realised by the alteration in the usual formula for the ordinary metre bridge: $\frac{P}{Q} = \frac{1000 + (x_1 - x_2)}{1000 - (x_1 - x_2)}$, the formula for the present bridge being $\frac{P}{Q} = \frac{3812 + (x_1 - x_2)}{3812 - (x_1 - x_2)}$.

The Electrolytic Cell.—Two forms were tried, but the U-form was relinquished in favour of the straight one, shown in position in the bath (Fig. 2). This has one fixed and one movable electrode. The platinum wire from the fixed electrode, which is made of stout platinum sheet, passes downwards and is fused through the glass, and thence through the cork, *g*, by the side of the glass tube used for emptying the cell, to the binding screw. The wire from the movable electrode is fused into a tube closed at its lower end and containing a little mercury. The connecting wire, amalgamated at its lower end, passed in at the top of this tube, where the binding screw *d* is seen, and dips into the mercury at *e*. This tube works smoothly in a slightly larger one, *ab*, fixed at *b*. When the inner tube is lifted up, a steel rod is inserted between the upper end of the fixed outer tube and a brass disk, seen edgewise at *a* and fastened to the cork *f*, which serves as a handle for raising the electrode. In the illustration, the electrodes are in the closed position. The length of the steel rod is therefore equivalent to the mean distance between the electrodes.

After calibration, the electrodes were coated with platinum-black by the electrolysis of platinum tetrachloride as recommended by Kohlrausch.

The results obtained are collected in the table on page 64.

Percentage concentration.	Equivalents per litre.	Specific resistance.	$K_0^0 \times 10^4$. Specific conductivity.	Molecular conductivity.	Dissociation values.
1·4	0·43	71·435	140·0	97·50	40·63
2·87	0·89	39·484	253·3	85·20	35·50
5·28	1·66	23·553	424·5	76·60	31·92
16·09	5·37	12·401	806·4	44·91	18·71
22·60	7·96	9·978	1002·2	38·32	15·97
30·71	11·20	7·803	1281·6	34·43	14·35
33·75	12·53	7·266	1376·3	32·94	13·72
36·08	13·58	6·938	1441·3	31·83	13·26
38·49	14·71	6·853	1459·2	29·77	12·40
43·26	17·03	6·704	1491·6	26·28	10·95
48·90	19·91	6·921	1444·9	21·77	9·07
52·83	22·06	7·272	1375·0	18·70	7·79
53·22	22·27	7·391	1353·1	18·23	7·60
65·72	29·92	9·779	1022·6	10·30	4·29
71·29	33·76	12·697	787·6	7·00	2·92
74·99	36·45	16·430	607·6	4·99	2·08
79·21	39·69	21·366	468·0	3·54	1·48
82·22	42·08	24·670	405·5	2·89	1·20
92·07	50·42	45·388	220·3	1·31	0·55
93·52	51·73	57·518	173·9	1·01	0·42
100 03	57·69	71·134	140·6	0·73	0·30

In Fig. 3 are shown the curves for the conductivities of various acids as compared with phosphoric acid.

Summary of Conclusions.

1. Pure phosphoric acid is obtained by hydrating re-distilled phosphorus trichloride slowly, keeping the temperature of the reaction low, heating to expel hydrochloric acid, and oxidising with pure dilute nitric acid.

2. The most trustworthy means of analysis of phosphoric acid are:
   - *a.* by the usual magnesium method, which is capable of great accuracy.
   - *b.* by heating the solution with pure lead monoxide in a platinum crucible until all the water has been expelled.

3. A very accurate form of Wheatstone bridge can be made by an air-line of platinum-iridium wire of half a metre in length, the "bridge-ends" being lengthened by a subsidiary wire of manganin alloy running parallel to the main wire to the middle of the bridge and back again. The slider is most convenient when mounted to run between the scale and the wire, and capable of rocking through a small arc from scale to wire.

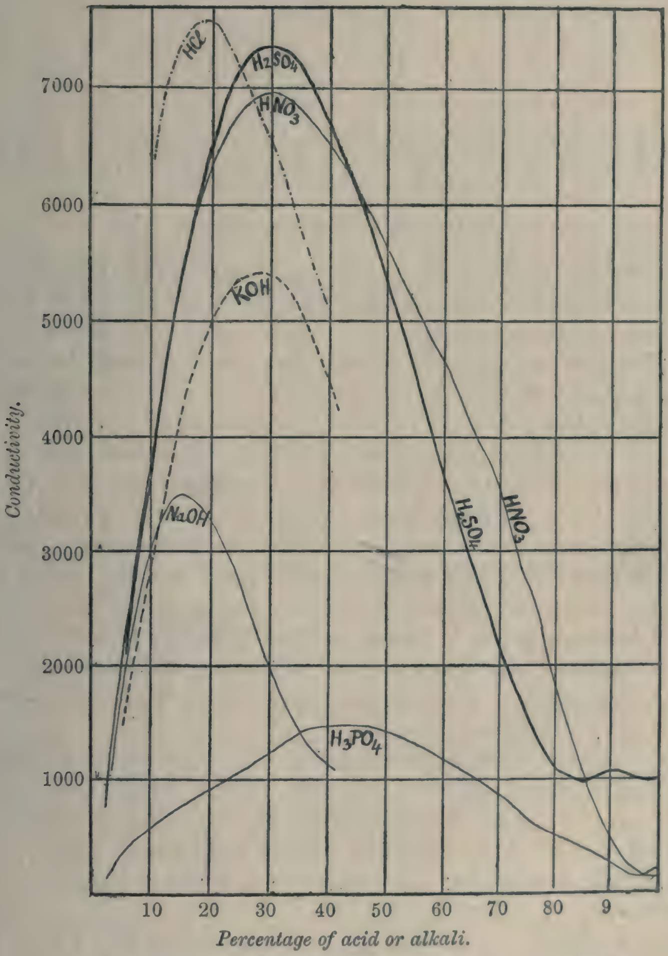
4. The conductivity measurements seem to bear out the theory of indicators regarding the ionisation of the hydrogen atoms in the molecule of phosphoric acid.

5. The conductivity of phosphoric acid increases with the concentration from 1·4 per cent. to about 38 per cent.; thence to 44 per cent.

it increases more slowly; it then decreases slowly to about 50 per cent., after which the decrease is as rapid as the former rise.

The author gratefully acknowledges the help continually received from Mr. Manley, Daubeny Curator, Magdalen College Laboratory, throughout the progress of this research, and would also express his sincerest thanks to the President and Fellows of Magdalen College for permission so willingly given to work in their well-equipped

FIG. 3.



Conductivities of common mineral acids and alkalis compared.

laboratory. He has also to thank his friend and former tutor, Dr. Veley, at whose suggestion the whole work was attempted, for encouragement and advice, and the Chemical Society for a grant of money towards the expense of the research.

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IX.—*The Molecular Volumes of the Nitrites of Barium, Strontium, and Calcium.*

By Prafulla Chandra Rây.

In continuation of my previous investigation (Trans., 1908, **93**, 997), the determination of the molecular volumes of the nitrites of barium, strontium, and calcium has been undertaken. As these nitrites crystallise with one molecule of water, two sets of results have been obtained, namely, those of the hydrated and of the anhydrous compounds. Incidentally, the molecular volumes of the water of crystallisation of a class of well-defined monohydrated salts have also been ascertained.

The preparation of these nitrites has already been described (Trans., 1905, **87**, 178). It is only necessary to add here that, owing to the deliquescent nature of these salts, special precautions were taken in handling them. Calcium nitrite caused great trouble in the damp climate of Calcutta. Although this salt was quickly pressed between folds of bibulous paper to remove adhering mother liquor, it always gave a variable and much higher percentage of water than that required by theory. After several unsuccessful trials, the following method gave satisfactory results:

The substance, dried as above, was placed overnight in a desiccator containing sulphuric acid of sp. gr. 1·625. Barium nitrite under similar treatment also yielded the monohydrated salt. The salts were dehydrated at 108—110°. Calcium nitrite, when dried at 110°, proved to be faintly alkaline, but the estimation of nitrogen agreed with the theoretical value.

Barium Nitrite.—Three distinct preparations gave $H_2O = 7·67$, 7·70, and 7·50 respectively. $Ba(NO_2)_2,H_2O$ requires $H_2O = 7·29$ per cent. The anhydrous salt gave $Ba = 59·82$, the calculated amount being 59·83 per cent. It may be mentioned here that Arndt stated that, even at 110°, barium nitrite is not readily dehydrated (*Zeitsch. anorg. Chem.*, 1907, **27**, 355). The specific gravity of the hydrated salt was found to be 3·185 at 27°; that of a second preparation was 3·162 at

31°, the mean value being 3·173. The specific gravity of the anhydrous salt was 3·232 at 23°; a second preparation gave 3·228 at 23°; mean = 3·23. Slight variations in the degree of hydration often cause considerable disparity in the value.

Strontium Nitrite.—The percentage of strontium in the monohydrated salt was 44·06, the calculated amount being 44·25. The mean of two fairly concordant determinations of the hydrated salt gave 2·645 at 27° as the specific gravity, whilst that of the anhydrous salt was 2·867.

Calcium Nitrite.—The estimation of water in several samples gave $H_2O = 11·97$, 11·55, 11·80, and 12·50. $Ca(NO_2)_2,H_2O$ requires $H_2O =$ 12·00 per cent. The specific gravities of two distinct preparations of the hydrated salts were found to be 2·225 and 2·237 respectively at 34°; mean = 2·231. The specific gravities of two samples of the anhydrous salt were 2·286 and 2·302; mean = 2·294. The molecular volumes of the salts * calculated from their specific gravity determinations are presented below in a tabulated form:

Name of salt.	Mol. wt.	Sp. gr.	Mol. vol.
$Ba(NO_2)_2,H_2O$	247	3·173	77·87
$Ba(NO_2)_2$	229	3·230	70·90
	Diff. (mol. vol. of H_2O)		6·97
$Sr(NO_2)_2,H_2O$	197·3	2·645	74·59
$Sr(NO_2)_2$......................	179·3	2·867	62·54
	Diff. (mol. vol. of H_2O)		12·05
$Ca(NO_2)_2,H_2O$	150	2·231	67·24
$Ca(NO_2)_2$	132	2·294	57·56
	Diff. (mol. vol. of H_2O)		9·68

It is evident that the above nitrites, even in the anhydrous state, unlike the anhydrous magnesium sulphates, have not identical molecular volumes, but the latter values appear to be functions of the atomic weights of the corresponding element. The molecular volume of the water of crystallisation also varies, being least in barium nitrite and greatest in strontium nitrite. This is no doubt due to the fact that the water molecules are held with varying degrees of tenacity in the three compounds. According to Kopp's conclusion, however, in salts containing only a small number of water molecules (1 to 3), the molecular volume is a constant number, namely, 12·4.

If the molecular volumes of the nitrites are deducted from the corresponding volumes of the nitrates, the remainder is approximately constant. Potassium and sodium nitrites have been left out of consideration as their molecular volumes are abnormal, as pointed out in the previous paper (*loc. cit.*, 1000). Thus:

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* Magnesium nitrite could not be included in this series as the salt crystallises with three molecules of water, and when it is kept in a vacuum over sulphuric acid, it parts with only one molecule (compare Rây, Trans., *loc. cit.*, 779).

Salt.	Mol. vol.	Diff. (for O_2).	Diff. (for O).
$Ba(NO_3)_2$	80·8*	9·9	4·95
$Ba(NO_2)_2$	70·9		
$Sr(NO_3)_2$	70·91	8·37	4·19
$Sr(NO_2)_2$	62·54		
$Ca(NO_3)_2$	65·60	8·04	4·02
$Ca(NO_2)_2$	57·56		
$(AgNO_3)_2$	78·08	8·92	4·46
$(AgNO_2)_2$	69·16		
		Mean	4·40

According to Kopp the radicle NO_3 occupies a constant volume, namely, 28·6, in the nitrates of barium, strontium, silver, potassium, and sodium (Thorpe, *Kopp Memorial Lecture*, Trans., 1893, **63**, 800). It may safely be assumed that calcium nitrate also comes under this category.

As it has just been shown that the increments in volume due to the accession of an atom of oxygen are approximately constant ($=4·4$), we get $28·6 - 4·4 = 24·2$ as the average volume of the radicle of the nitrite, NO_2, of these metals. As early as 1840, Kopp pointed out that in the salts of the metals of the alkalis and alkaline earths, the "primitive atomic volumes" of the metals are not retained, although in the compounds of the heavy metals, for example, silver and mercury, the latter retain their original volumes. If we deduct from the molecular volumes of the nitrates the constant 28·6, we get the following values for the atoms of the respective metals: $Ba = 23·60$, $Sr = 13·71$, $Ca = 8·40$, and $Ag = 10·44$.

Now the original atomic volumes of barium, strontium, and calcium are 36·5, 34·9, and 25·4 respectively. One cannot help being struck with the fact that the latter bear a simple proportion to the former. Thus barium in its compounds occupies two-thirds the original atomic volume, whilst strontium and calcium occupy nearly one-third of the same. Considering the difficulties in the way of preparing these metals in the pure shape, closer approximation cannot be expected. The radicle NO_2 in the liquid condition has the volume 32·0 (Thorpe,

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* The molecular volumes have been calculated from the specific gravities as given in Erdmann-Kothner's *Natur-Konstanten*, 1905. Although the authors give no reference to the names of the observers, they have evidently placed greater reliance on the determinations by Favre and Valson (*Compt. rend.*, 1873, **77**, 802) than on those by Filhol. The specific gravities as found by the latter are often too low. Thus, the specific gravity of $Ca(NO_3)_2$ is given as 2·0, whereas, according to Favre and Valson, it is 2·5. Filhol's number is untrustworthy on the face of it.

Trans., 1880, **37**, 382). We have seen above that in the nitrites of the alkaline earths and of silver, the radicle NO_2 occupies the volume 24·2, or almost exactly three-fourths of the former. Prideaux has recently shown that the atomic volume of liquid phosphorus is 20·0, whilst in the case of quinquevalent and tervalent phosphorus the values are 15·10 and 25·06 respectively (Trans., 1907, **91**, 1715). Here, also, a very simple relationship is noticeable. It is scarcely probable that so many striking coincidences should be purely accidental. An interesting problem suggestive of a *law of proportionality* seems to be opened up. Indeed, the assumptions made by Schröder, Hermann (*J. pr. Chem.*, 1876, [ii], **13**, 28), and E. Wilson (*Proc. Roy. Soc.*, 1881, **32**, 457) need a careful reconsideration.

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X.—*Organic Derivatives of Silicon. Part. IX. Experiments on the Resolution of* dl-*Benzylethylpropyl*iso*butylsilicanesulphonic Acid.*

By FREDERIC STANLEY KIPPING and HAROLD DAVIES, A.I.C.*

IN part III of these investigations (Trans., 1907, **91**, 717) an account was given of the synthesis of *dl*-benzylmethylethylpropylsilicane, $SiMeEtPr·CH_2·C_6H_5$, of the conversion of this silicohydrocarbon into its sulphonic derivative, $SiMeEtPr·CH_2·C_6H_4·SO_3H$, and of experiments on the resolution of this acid into its optically active components. Although in these experiments seven different salts, prepared from the *dl*-acid and an optically active base, were submitted to systematic fractional crystallisation, the results were negative and, except in one instance, which is referred to below, not the slightest indication of a resolution of the acid was obtained. As this might be due to the close similarity of the three alkyl radicles in the asymmetric silicon group, it seemed advisable to prepare and to examine a *dl*-sulphonic acid of the same type but containing three radicles less closely related than are the three normal homologous alkyls in benzylmethylethylpropylsilicanesulphonic acid. The results of this work are recorded below.

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* Mr. W. E. Bullock, B.Sc., took part in the earlier stages of this work, and before leaving to undertake other duties, he had prepared and analysed the silicohydrocarbon, its sulphonic derivative, and the menthylamine salt of the sulphonic acid. The investigation was continued from this stage in conjunction with Mr. H. Davies.

dl-*Benzylethylpropyl*iso*butylsilicane*, $SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_5$, was prepared by treating benzylethylpropylsilicyl chloride with magnesium *iso*butyl bromide; it is a colourless liquid having the character of a hydrocarbon, and boils at 282—283° under atmospheric pressure.

dl-*Benzylethylpropyl*iso*butylsilicanesulphonic acid*,

$$SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H,$$

was then obtained by sulphonating the silico-hydrocarbon with chlorosulphonic acid under the conditions previously described in the case of the lower homologue (*loc. cit.*), and, having previous experience as a guide, little difficulty was met with in isolating this acid in the form of its *l*-menthylamine salt.

l-*Menthylamine* dl-*benzylethylpropyl*iso*butylsilicanesulphonate*,

$$SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N,2H_2O,$$

crystallises well from moist light petroleum in glistening leaflets, and although it is readily soluble in the moist solvent, the anhydrous salt dissolves much more freely in absence of water; it is very similar in most respects, not only to its lower homologue, but also to the corresponding salt of benzylethyldipropylsilicanesulphonic acid (Marsden and Kipping, Trans., 1908, **93**, 205), a fact which seems to show that the *d*A*l*B and *l*A*l*B-components of the salts formed from the two *dl*-acids are both very similar to the single salt of the dipropyl derivative, which contains no asymmetric silicon group.

The *l*-menthylamine salt of *dl*-benzylethylpropyl*iso*butylsilicanesulphonic acid is not resolved into its components when it is systematically crystallised from moist light petroleum or from aqueous methyl alcohol; it is very useful, however, as a means of isolating the acid from the crude product of sulphonation of the silico-hydrocarbon, and also as a means of identifying the acid.

In the experiments on the resolution of the *dl*-acid, it was necessary to start from a preparation of known purity; for this reason the sodium salt of the *dl*-acid was always prepared from the pure *l*-menthylamine salt and then precipitated directly with the hydrochloride of the active base.

The *strychnine*, *brucine*, *cinchonidine*, *quinine*, and *cinchonine* salts were thus prepared, and from the last-named three compounds the corresponding alkaloidal *hydrogen* salts were also obtained by treating the normal salts with hydrochloric acid (compare Trans., 1907, **91**, 233). These eight substances were separately and systematically crystallised from various solvents under different conditions, and the extreme fractions thus obtained were then examined. In all cases, except in that of the cinchonine hydrogen derivative, the melting or decomposing points and specific rotations of these extreme fractions of a given salt were identical within the limits of probable experimental error.

Although these facts might seem to be sufficient to show that the *dl*-acid had not been resolved in any of these experiments, it was not impossible that the salts of the *d*- and *l*-acids, like many of those of *d*- and *l*-sulphobenzylethylpropylsilicyl oxides (Trans., 1908, **93**, 457), might be so similar in melting point and in specific rotation as to be practically indistinguishable; for this reason it was thought advisable, in many cases, to convert the two samples of the alkaloidal salt separately into the *l*-menthylamine derivative and to compare the two specimens of the latter with the original *l*-menthylamine salt of the *dl*-acid; this test also failed to afford any evidence of the resolution of the acid.

The one salt which showed an exceptional behaviour was the cinchonine hydrogen derivative. On crystallising this compound systematically from aqueous alcohol and then recrystallising the two extreme fractions once from ethyl acetate (containing a little methyl alcohol), two colourless samples were obtained; these, when dried at 100°, showed a difference in melting point of about 5°, to which, however, little importance could be attached, as the 'most soluble' fraction melted at the lower temperature and might contain traces of impurity. When examined polarimetrically in methyl-alcoholic solution, however, a difference, which could not be due to experimental error, was observed, the 'most readily soluble' fraction giving $[\alpha]_D + 61\cdot6°$, the other $[\alpha]_D + 72\cdot7°$. After one recrystallisation from ethyl acetate (and methyl alcohol) these values became $+57\cdot1°$ and $73\cdot8°$ respectively and the decomposing points of the two fractions were then identical (220—223°).

These specimens having been placed aside, the next 'most readily soluble' fraction of the salt was examined; this gave $[\alpha]_D + 62\cdot5°$ and decomposed at the same temperature (220—223°) as the other portions.

These results seemed to show that the *dl*-acid had been resolved, but unfortunately the further examination of these fractions failed to establish this inference; when separately converted into the *l*-menthylamine salt and also into the normal cinchonidine salt, the two extreme fractions gave, in both cases, products which, so far as could be ascertained, were identical with one another, and also with the corresponding salts of the original *dl*-acid.

The observed difference in specific rotation of the fractions of this cinchonine hydrogen salt has not yet been accounted for. The compound was prepared from a sample of the normal cinchonine salt, and as the latter had been obtained originally by converting the pure *l*-menthylamine salt into the sodium salt and precipitating with cinchonine hydrochloride, it could hardly have been impure; further, the purity of the normal cinchonine salt, and at the same time that of the base contained in it, had been established by the fact that the two extreme fractions resulting from the systematic crystallisation of the preparation were identical in melting point and in specific rotation. It seemed, therefore, that the only possible impurity in the cinchonine hydrogen derivative might be some unchanged normal cinchonine salt; but the latter has a high specific rotation, $[\alpha]_D$ +110°, and if present would doubtless pass into the mother liquors and thus raise the specific rotation of the more soluble fractions of the hydrogen salt, so that the low values obtained for the latter could not be explained on this basis.

Even, in spite of these considerations, if the results of the crystallisation of the cinchonine hydrogen salt had stood alone, they might possibly have been passed over and attributed to some undiscovered source of error, but as a matter of fact very similar and quite independent observations were made some time ago by one of us during the examination of the corresponding salt of benzylmethylethylpropylsilicanesulphonic acid (Kipping, Trans., 1907, **91**, 717). The cinchonine hydrogen salt of this acid, systematically crystallised from aqueous alcohol and then from anhydrous acetone containing a trace of water, gave extreme fractions of almost identical melting point, but in methyl-alcoholic solution the specific rotation of the 'most readily soluble' fraction was +75·1°, and that of the 'most sparingly soluble' fraction +64·9°; after further crystallisation, two corresponding fractions having $[\alpha]_D$ +77·4° and +65·3° respectively were obtained. The difference is of the same order as that observed in the case of the *iso*butyl compound, but in these experiments the more soluble fractions have the higher rotation. The 'most readily soluble' fraction, having $[\alpha]_D$ +77·4° (see above), was converted into the sodium, and then into the *l*-menthylamine salt, and the latter was recrystallised from moist light petroleum in order to separate traces of cinchonine; it melted at 116—122°, and seemed, therefore, to be a slightly impure specimen of the salt of the *dl*-acid which melts at 122—123°.

These results were not recorded in describing the experiments on the crystallisation of cinchonine hydrogen benzylmethylethylpropylsilicanesulphonate (*loc. cit.*) because, on trying to confirm them with a totally different preparation, the two extreme fractions of the salt were found to have the same specific rotations within the limits of experimental error. The matter, however, has now assumed another aspect; the observed differences in specific rotation are in both cases so large as to exclude any possibility of their being due to error in the polarimetric readings, and the melting or decomposing points of the fractions of different specific rotation are so nearly identical that it is difficult to believe that they contain impurity. On the whole, it seems possible that the cinchonine hydrogen salts are really resolved under certain conditions, but that the enantiomorphous relationship of the two optically active acids is even more difficult to establish than in the case of the *d*- and *l*-forms of sulphobenzylethylpropylsilicyl oxide (*loc. cit.*). This possibility will be further examined as soon as a fresh supply of one of the *dl*-acids has been obtained.

EXPERIMENTAL.

*Benzylethylpropyl*iso*butylsilicane*, $SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_5$.

In preparing this silico-hydrocarbon, benzylethylpropylsilicyl chloride (Trans., 1907, **91**, 722) was treated with an ethereal solution of magnesium *iso*butyl bromide, and as no reaction seemed to occur at the ordinary temperature, the ether was evaporated and the residue heated at about 140° during three hours. After cooling, and adding water, the crude product was separated and distilled under diminished pressure. The principal fraction was then heated with sodium until no further action occurred, and was finally submitted to fractional distillation under atmospheric pressure; it was thus obtained as a colourless, mobile, refractive liquid boiling at 282—283°, the yield of the pure compound being about 60 per cent. of the theoretical:

0·1596 gave 0·4503 CO_2 and 0·1654 H_2O. C = 77·0; H = 11·5.
0·2617 „ 0·7443 CO_2 „ 0·2740 H_2O. C = 77·1; H = 11·5.
$C_{16}H_{28}Si$ requires C = 77·4; H = 11·3 per cent.

Sulphonation of the Silico-hydrocarbon.—The behaviour of benzylethylpropyl*iso*butylsilicane towards concentrated sulphuric acid was not investigated, as it seemed probable that the sulphonic derivative would be obtained far more easily with the aid of chlorosulphonic acid (compare Trans., 1907, **91**, 739); employing this reagent, and proceeding just as described in the case of benzylmethylethylpropyl silicane, sulphonation is accomplished without difficulty, and a clear, slightly fluorescent, aqueous solution of the crude ammonium salt is ultimately obtained.

The acid is most conveniently isolated in the form of its *l*-menthylamine salt, which is precipitated as an oil on adding excess of menthylamine hydrochloride to the solution of the ammonium salt. The precipitate slowly solidifies to a pasty mass, which is first pressed on porous earthenware, and then fractionally crystallised from light petroleum (b. p. 40—50°) to which a few drops of water are added; after many crystallisations, the pure salt was obtained in colourless plates, but a considerable proportion of the crude product remained in the mother liquors as an oil, which has not yet been investigated. The yield of the pure compound is poor compared with that obtained in the sulphonation of benzylmethylethylpropylsilicane.

l-*Menthylamine* dl-*Benzylethylpropyl*iso*butylsilicanesulphonate*, $SiEtPr(C_4H_9)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$.

This salt is indistinguishable in appearance from that of its lower homologue, which it resembles in every respect, so that a detailed description is unnecessary. It crystallises well from moist light petroleum, but does not separate even from very highly concentrated solutions in absence of water; the hydrated crystals liquefy far below 100°, the anhydrous salt melting at 127—128°:

3·196, of air-dried salt, lost 0·2238 at 100°. $H_2O = 7{\cdot}0$.

$C_{26}H_{49}O_3NSSi,2H_2O$ requires $H_2O = 6{\cdot}9$ per cent.

0·1848 gave $C = 64{\cdot}2$; $H = 10{\cdot}3$.*

0·1866 ,, $C = 64{\cdot}1$; $H = 10{\cdot}4$.

0·1676 ,, $C = 64{\cdot}2$; $H = 10{\cdot}4$.

$C_{26}H_{49}O_3NSSi$ requires $C = 64{\cdot}6$; $H = 10{\cdot}1$ per cent.

The equivalent of the anhydrous salt was determined by the method previously described (*loc. cit.*, p. 736) and was found to be 484, the calculated value being 483.

The molecular weight was also determined by the ebullioscopic method in methyl-alcoholic solution:

Substance.	Weight of solvent.	*E.*	M.W.
0·469	20·2	0·080	243
0·666	20·2	0·105	264
0·328	16·0	0·070	280
0·894	16·0	0·160	294
1·419	16·0	0·235	316

Although the isolation of this menthylamine salt necessitates repeated fractional crystallisation from moist light petroleum, the compound is not thereby resolved into its optically active components; this statement is based on the very close resemblance between this salt and the corresponding derivative of its lower homologue, and also on the fact that the aqueous solution of the sodium salt prepared from it shows no visible optical activity.

Metallic Salts of dl-*Benzylethylpropyl*iso*butylsilicanesulphonic Acid.*— The solution of the *sodium* salt, prepared from the pure *l*-menthylamine derivative by adding a very slight excess of sodium carbonate and then distilling the menthylamine in a current of steam, has a very soapy nature and froths in a very troublesome manner during the steam distillation. When neutralised with acetic acid and evaporated, the sodium salt separates as a soapy mass which, after several days, becomes flaky and apparently crystalline; on filtering, however, the salt remains as a paste which, under the microscope, is seen to consist of oily globules. Although readily soluble in water, the salt is precipitated on addition of other salts, such as sodium carbonate, to its concentrated aqueous solution.

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* Mr. Bullock's rough note-book, in which the weights of the CO_2 and H_2O respectively were recorded, has been mislaid; the above data were supplied to me at the time the combustions were made.—F. S. K.

The solution of the *ammonium* salt of the sulphonic acid, prepared by decomposing some of the alkaloidal salts with ammonia, is very similar to that of the sodium salt.

The *barium* salt is precipitated in flocculent masses from a solution of the sodium salt, and is only very sparingly soluble in cold water, but dissolves freely in warm aqueous alcohol.

Cinchonidine dl-*Benzylethylpropyl*iso*butylsilicanesulphonate.*

This salt was prepared by treating the neutral aqueous solution of the sodium salt with excess of a solution of cinchonidine hydrochloride; the oily precipitate, which soon solidified, was washed well with water and fractionally crystallised from aqueous alcohol; after six crystallisations the two extreme fractions melted simultaneously at 184°.

These two fractions were then recrystallised once from ethyl acetate, dried at 100°, and examined polarimetrically in methyl-alcoholic solution.

'Most soluble' fraction.—0·573, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3{\cdot}18°$; whence $[\alpha]_D - 69{\cdot}4°$.

'Least soluble' fraction.—0·599, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 3{\cdot}28°$; whence $[\alpha]_D - 68{\cdot}6°$.

The cinchonidine salt is very readily soluble in the common alcohols, and in chloroform; it crystallises well, in lustrous needles or prisms, from acetone, ethyl acetate, benzene, or ether; it is only very sparingly soluble in hot water.

Cinchonidine Hydrogen Salt.

This compound, prepared by treating the normal salt with excess of hydrochloric acid in alcoholic solution and then precipitating with water, was deposited as an oil which rapidly solidified; after having been washed with water it was crystallised seven times from aqueous alcohol. The extreme fractions, when dried at 100°, began to decompose at about 210°, liquefying simultaneously at about 218°; their specific rotations were determined in methyl-alcoholic solution.

'*Most soluble' fraction.*—0·866, made up to 25 c.c. in a 2-dcm. tube, gave α $-3·17°$; whence $[\alpha]_D$ $-45·8°$.

'*Least soluble' fraction.*—0·920, made up to 25 c.c. in a 2-dcm. tube, gave α $-3·33°$; whence $[\alpha]_D$ $-45·2°$.

The cinchonidine hydrogen salt crystallises well from aqueous alcohol and from aqueous acetone in lustrous plates. It is sparingly soluble in anhydrous acetone or ethyl acetate, much more readily so in presence of traces of water; it is very soluble in chloroform, but practically insoluble in benzene, ether, or petroleum.

Strychnine dl-*Benzylethylpropyl*iso*butylsilicanesulphonate.*

The strychnine salt, obtained directly from the sodium salt as an oil, did not solidify even on keeping for some time; it was washed with very dilute alcohol, and the milky liquid decanted. In the course of twenty-four hours these washings deposited the salt in glistening plates, but on trying to crystallise the main portion of the salt from aqueous alchohols of different concentrations, it was invariably deposited as an oil; attempts to recrystallise a portion of the crystalline compound were equally unsuccessful, as, in spite of cooling and "seeding," the salt remained a liquid. The small sample of crystalline compound melted indefinitely from about 86—95°, owing to the presence of water of crystallisation, but after having been dried at 100° its melting point was 236—238°.

Although this compound, like so many of the alkaloidal salts of these silicanesulphonic acids, remains oily in presence of aqueous solvents, it crystallises well and readily from anhydrous acetone. It was therefore systematically treated with this solvent, and after eight operations the two extreme fractions were examined. The 'most soluble' one melted at 226—227°, the other at 237—238°, and their specific rotations, determined in methyl-alcoholic solution, were practically identical:

'*Most soluble' fraction.*—0·542, made up to 25 c.c. in a 2-dcm. tube, gave α $-0·34°$; whence $[\alpha]_D$ $-7·9°$.

'*Least soluble' fraction.*—0·620, made up to 25 c.c. in a 2-dcm. tube gave α $-0·38°$; whence $[\alpha]_D$ $-7·6°$.

As their specific rotations were very low, and the experimental error might be large, the 'least soluble' fraction was decomposed with ammonia and converted into the *l*-menthylamine salt, which was then recrystallised from moist light petroleum; the melting point of this preparation was identical with that of the salt of the *dl*-acid, namely, 127—128°.

The low melting point of the 'most soluble' fraction was doubtless due to the presence of a trace of impurity formed by the decomposition of the salt during repeated crystallisation, as when recrystallised once its melting point rose to 235—237°.

Brucine dl-*Benzylethylpropyl*iso*butylsilicanesulphonate.*

This salt was prepared by decomposing the cinchonidine hydrogen compound with ammonia and then precipitating the neutral solution of the ammonium salt with excess of brucine hydrochloride; the oily product, which soon solidified, was washed well with water, and systematically crystallised from aqueous alcohol, from which it separated in lustrous, very bulky masses of needles.

After nine operations, the extreme fractions were dried at 100°, and separately recrystallised from ethyl acetate; they then melted simultaneously at 163°, and had the same specific rotation in methyl-alcoholic solution within the limits of experimental error:

'*Most soluble*' *fraction.*—0·657, made up to 25 c.c. in a 2-dcm. tube, gave α $-0·33°$; whence $[\alpha]_D$ $-6·27°$.

'*Least soluble*' *fraction.*—0·618, made up to 25 c.c. in a 2-dcm. tube, gave α $-0·30°$; whence $[\alpha]_D$ $-6·07°$.

During the crystallisation of this salt from aqueous alcohol and anhydrous ethyl acetate, it seemed that a resolution had occurred, as different fractions melted at different temperatures; it was found, however, that this behaviour was due to dimorphism. Samples of the salt, crystallised from aqueous alcohol and then dried at 100°, melted at 141—144°; but when such samples were crystallised two or three times from anhydrous ethyl acetate without removing any of the salt or leaving any appreciable quantity in solution, the melting point rose to 161—163° and became constant. On the other hand, when samples melting at 161—163° were recrystallised from aqueous alcohol they melted at 141—144°.

Quinine dl-*Benzylethylpropyl*iso*butylsilicanesulphonate.*

For the preparation of this compound, a solution of the ammonium salt of the *dl*-acid, obtained by decomposing the strychnine salt, was employed, and excess of quinine hydrochloride. The product crystallised well from aqueous acetone in bulky masses of needles, but its solution in aqueous alcohol often gave oily deposits; it also crystallised well from a mixture of ethyl acetate and ether.

It was systematically crystallised from aqueous acetone; the two extreme fractions then melted simultaneously at 168—171°, and had practically the same specific rotation in methyl-alcoholic solution:

'*Most soluble*' *fraction.*—0·538, made up to 25 c.c. in a 2-dcm. tube, gave α $-4·71°$; whence $[\alpha]_D$ $-109·5°$.

'*Least soluble' fraction.*—0·597, made up to 25 c.c. in a 2-dcm. tube, gave α $-5{\cdot}38^\circ$; whence $[\alpha]_D$ $-112{\cdot}6^\circ$.

The salt is very readily soluble in the common alcohols, moist ethyl acetate, moist acetone, chloroform, or benzene, but practically insoluble in light petroleum.

Quinine Hydrogen Salt.

The decomposition of the normal salt with hydrochloric acid was carried out in the usual manner, and after washing well to remove quinine hydrochloride the product was systematically crystallised from aqueous acetone, from which it separated in bulky masses of needles; after many operations, the two extreme fractions were collected and dried at 100°. They both showed signs of decomposing at about 200°, and liquefied simultaneously at about 212°; their specific rotations were determined in methyl-alcoholic solution:

'*Most soluble' fraction.*—0·531, made up to 25 c.c. in a 2-dcm. tube, gave α $-3{\cdot}60^\circ$; whence $[\alpha]_D$ $-84{\cdot}7^\circ$.

'*Least soluble' fraction.*—0·466, made up to 25 c.c. in a 2-dcm. tube, gave α $-3{\cdot}09^\circ$; whence $[\alpha]_D$ $-82{\cdot}9^\circ$.

This salt separates as an oil from aqueous alcohol unless the proportion of water is very large; it is practically insoluble in dry ethyl acetate or benzene, and only sparingly soluble in dry acetone, from which it separates in poorly-defined crystals. It dissolves freely in chloroform and in the common alcohols.

Cinchonine dl-*Benzylethylpropyl*iso*butylsilicanesulphonate.*

This salt was prepared by treating a neutral solution of the pure sodium salt with excess of cinchonine hydrochloride; the oily precipitate soon solidified and was washed well with water. The salt was then systematically crystallised from aqueous methyl alcohol and the two extreme fractions were examined; they melted simultaneously and had the same specific rotation in methyl-alcoholic solution:

'*Most soluble' fraction.*—0·4785, made up to 25 c.c. in a 2-dcm. tube, gave α $+4{\cdot}19^\circ$; whence $[\alpha]_D$ $+109{\cdot}4^\circ$.

'*Least soluble' fractian.*—0·445, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha+3{\cdot}94^\circ$; whence $[\alpha]_D+110{\cdot}7^\circ$.

This cinchonine salt separates from aqueous alcohol or aqueous acetone in silky needles; it is soluble in ethyl acetate and in anhydrous acetone, but it does not crystallise well from these solvents. The crystals deposited from aqueous solvents are hydrated and melt at about 70°, but the anhydrous salt melts at 139—141°.

Cinchonine Hydrogen Salt.

The normal cinchonine salt described above was treated with hydrochloric acid in alcoholic solution, and the hydrogen salt was then precipitated by adding water; the product quickly solidified and was washed with dilute hydrochloric acid and with warm water. It was then dissolved in alcohol and fractionally precipitated with water, these operations being repeated about six times in a systematic manner. The two extreme fractions were then separately dissolved in methyl alcohol, the solutions mixed with anhydrous ethyl acetate, and left to evaporate over sulphuric acid; the colourless deposits were finally separated and dried at 100° until constant.

The 'most soluble' fraction decomposed at 215—218°, the other at 220—223°, and their specific rotations in methyl-alcoholic solution were very different:

'*Most soluble' fraction.*—0·481, made up to 25 c.c. in a 2-dcm. tube, gave α $+2{\cdot}35°$; whence $[\alpha]_D$ $+61{\cdot}6°$.

'*Least soluble' fraction.*—0·523, made up to 25 c.c. in a 2-dcm. tube, gave α $+3{\cdot}04°$; whence $[\alpha]_D$ $+72{\cdot}7°$.

The 'most soluble' fraction was next recrystallised once from a mixture of methyl alcohol and ethyl acetate, leaving a fair proportion of the salt in the mother liquors: this specimen was dried at 100° until constant; it then decomposed at 220—223°, and had a lower specific rotation than the sample from which it had been prepared:

0·3192, made up to 16 c.c. in a 2-dcm. tube gave, α $+2{\cdot}28°$; whence $[\alpha]_D$ $+57{\cdot}1°$.

The 'least soluble' fraction was fractionally precipitated from its alcoholic solution by adding water, and after several operations the 'least soluble' portion was collected, recrystallised from a mixture of methyl alcohol and ethyl acetate, and dried at 100°; it decomposed at 220—223°:

0·5095, made up to 25 c.c. in a 2-dcm. tube, gave α $+3{\cdot}01°$; whence $[\alpha]_D$ $+73{\cdot}8°$.

The melting point of the 'most soluble' fraction being identical with that of the very highly purified 'least soluble' fraction, almost excluded the possibility that the low specific rotation of the former might be due to impurity, but as a further precaution a sample of the salt, next in order to the 'most soluble' fraction, was recrystallised once from methyl alcohol and ethyl acetate, and dried at 100°; this specimen decomposed at 220—223°, and its specific rotation was almost as low as the 'most soluble' portion.

0·532 made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 2{\cdot}66°$; whence $[\alpha]_D$ $+62{\cdot}5°$.

It is perhaps unnecessary to add that, as the specific rotation of these salts might vary considerably in different samples of methyl alcohol containing variable proportions of water, the same sample of methyl alcohol was employed in all these determinations.

The above results could only be explained by assuming that the *dl*-acid had been resolved into its optical isomerides; in order, if possible, to obtain further evidence in favour of this conclusion, the samples of the cinchonine hydrogen salt having the specific rotations +73·8° and +62·5° respectively were separately decomposed with ammonia, and the cinchonine was separated by filtration. The solution from the salt $[\alpha]_D$ +62·5° was examined in the polarimeter, but instead of being lævorotatory, as it might possibly have been, it was very feebly dextrorotatory, owing to the incomplete separation of the cinchonine; this difficulty occurs in the case of many of these salts, and the whole of the alkaloid is not removed without some trouble. For this reason, the neutral solutions of the ammonium salts were separately precipitated with *l*-menthylamine hydrochloride, and the *l*-menthylamine salts were then recrystallised from moist light petroleum; after dehydration, the salt obtained from the fraction $[\alpha]_D$ +73·8° melted at 125—126°; that from the fraction $[\alpha]_D$ +62·5° at 126—127·5°; a mixture of these two salts melted at 125—126°.

As the *l*-menthylamine salts of the *d*- and *l*-acids might have the same melting point, the two preparations, corresponding with the samples of cinchonine hydrogen salt $[\alpha]_D$ +73·8° and $[\alpha]_D$ +62·5° respectively, were separately decomposed with sodium carbonate and the menthylamine distilled in a current of steam; the neutral solutions of the sodium salts were then precipitated with cinchonidine hydrochloride, and the two samples of cinchonidine salt recrystallised first from aqueous alcohol and then from acetone containing a trace of water.

These two preparations melted simultaneously at 184° and had the same specific rotation ($[\alpha]_D$ −67·6° and $[\alpha]_D$ −68·0° respectively) in methyl-alcoholic solution.

Our thanks are due to the Government Grant Committee of the Royal Society for a grant in aid of this investigation.

UNIVERSITY COLLEGE,
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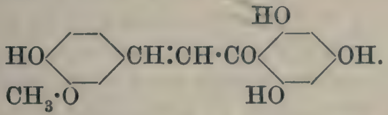
XI.—*Chemical Examination of Eriodictyon. Part II.*

By Frank Tutin and Hubert William Bentley Clewer.

The first part of this investigation of *Eriodictyon* leaves was carried out by one of us in conjunction with Dr. Power, and the results obtained were communicated to the meeting of the American Pharmaceutical Association held at Indianapolis in 1906 (*Proc. Amer. Pharm. Assoc.*, 1906, **54**, 352). In this communication it was shown that the leaves contain, besides essential oil, resins, and other amorphous products, a considerable amount of glucose, the hydrocarbons triacontane and pentatriacontane, formic, acetic, butyric, cerotic, and other acids, both in the free state and as glycerides, and a very small amount of a phytosterol. In addition to these products, three new crystalline substances of a phenolic nature were isolated, namely, eriodictyol, $C_{15}H_{12}O_6$ (m. p. 267°), homoeriodictyol, $C_{16}H_{14}O_6$ (m. p. 223°), and a very small amount of a substance possessing the formula $C_{16}H_{12}O_6$.*

In subsequent communications (Power and Tutin, Trans., 1907, **91**, 887; Proc., 1907, **23**, 243) the results of further work on eriodictyol and homoeriodictyol were described, and the latter substance was shown to possess the following constitution:



A further and larger amount of the extract of *Eriodictyon* leaves has now been worked up in order to obtain the requisite material for the continuation of experiments with eriodictyol and its homologue. During this process a quantity of the product has been accumulated, from which the small amount of the substance, $C_{16}H_{12}O_6$, was isolated. An exhaustive examination of this product has resulted in the isolation of a larger quantity of the last-mentioned compound, the formula and properties of which have been confirmed, together with two other crystalline substances of a phenolic nature, both of which are new compounds.

The substance which was previously isolated in small amount, and which it is now proposed to designate *chrysoeriol*, forms golden-yellow leaflets which do not melt at 337°. It has the formula $C_{16}H_{12}O_6$, and is present in the air-dried leaves to the extent of 0·0093 per cent. of their weight. It contains three hydroxyl groups, since it yields a *triacetyl* derivative, $C_{16}H_{11}O_6(\cdot CO\cdot CH_3)_3$, which melts at 211—212°.

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* In Abstr., 1906, **90**, ii, 885, the formula of this substance is incorrectly given as $C_{16}H_{41}O_6$.

The first of the newly-isolated compounds was obtained in an amount corresponding with 0·0187 per cent. of the weight of the air-dried leaves. It crystallises in yellow needles melting at 258°, and for it the name *xanthoeridol* is proposed. It possesses the formula $C_{18}H_{14}O_7$, and, like chrysoeriol, yields a *triacetyl* derivative (m. p. 175—176°).

The other new compound is represented by the formula $C_{19}H_{18}O_7$, and the amount of it present in the air-dried leaves is equivalent to 0·0117 per cent. of their weight. It forms long, pale yellow, flattened needles, which, after drying in the air, melt at 199°, and contain one molecule of water of crystallisation; the anhydrous substance melts at 209°. There are two substances of the formula $C_{19}H_{18}O_7$ which are stated to melt near 200°, namely, the methyl ester of usnolic acid (Widman, *Annalen*, 1902, **324**, 139), which melts at 202°, and quercetin tetramethyl ether (Kostanecki, Lampe, and Tambor, *Ber.*, 1904, **37**, 1404), which melts at 198°. It was readily ascertained that the compound we have isolated is not identical with methyl usnolate, since it yields a dark purplish-brown colour with ferric chloride, whilst the latter compound gives a green colour. The properties attributed to the tetramethyl ether of quercetin, however, are practically identical with those of the compound we have obtained, and it therefore appeared probable that the two substances might be identical. Through the courtesy of Professor Kostanecki, who supplied us with a specimen of tetramethylquercetin, we were enabled directly to compare the substances in question, when it was found that a mixture of the two preparations melted at about 160°. The substance from eriodictyon leaves is therefore a new compound, and it is proposed to designate it *eriodonol*. When treated with acetic anhydride, eriodonol yields a *tetra-acetyl* derivative (m. p. 131°), thus indicating the presence of four hydroxyl groups.

EXPERIMENTAL.

A quantity of the same alcoholic extract of the leaves of *Eriodictyon Californicum* (Hooker and Arnott), Greene, as had been employed in the first investigation, representing approximately 8580 grams of the air-dried leaves, was mixed with water and steam passed through the mixture for some time. The aqueous liquid was then decanted from the large amount of resin, and the latter again treated several times in a similar manner in order to free it as completely as possible from substances soluble in water. The combined aqueous extracts were then evaporated to a convenient bulk, and repeatedly extracted with ether. In the former investigation eriodictyol and homoeriodictyol were isolated from this ethereal extract by fractional extraction with a solution of sodium carbonate. It has now been ascertained that these substances are more conveniently obtained, and in better yield, when the ethereal liquid is first extracted with a solution of ammonium carbonate. This latter treatment removes from the ethereal solution a large amount of sticky, uncrystallisable matter of an acidic nature, from which nothing definite could be isolated. Extraction of the ethereal liquid with sodium carbonate solution then yields a precipitate of the monosodium compound of homoeriodictyol, and the filtrate from the latter, on acidification, gives a product consisting very largely of eriodictyol. This product has been exhaustively examined, but was found to contain no crystalline substance other than eriodictyol.

The large amount of resin referred to above, which had been freed from substances soluble in water, was mixed with purified sawdust and successively extracted in a Soxhlet apparatus with petroleum (b. p. 33—50°) and ether, but only the extract obtained by the latter solvent was examined in the present investigation. It was from this ethereal extract that the greater part of the homoeriodictyol was obtained, and here again the isolation of this substance is greatly facilitated by first removing from the ethereal liquid the substances soluble in a solution of ammonium carbonate.

On shaking the ethereal extract of the resins with a solution of ammonium carbonate, a very large quantity of the ammonium salt of an acidic resin separates in the form of a heavy, dark green tar, on the surface of which is a brown, aqueous layer. Nothing crystalline could be obtained from either of these products, the former yielding upwards of a kilogram of a nearly hard, green resin. The ethereal liquid, after considerable dilution, was then exhaustively extracted by shaking with successive portions of a solution of sodium carbonate. The large amount of the crystalline sodium compound of homoeriodictyol suspended in the alkaline liquids thus obtained was rapidly collected and washed, first with ether, and subsequently with a little water. The aqueous portion of the filtrate was then immediately acidified, as it rapidly absorbs oxygen on exposure to the air. The sodium compound was recrystallised from water, after which the mother liquors were acidified, and the precipitated product added to the material obtained on acidifying the original filtrate from the sodium derivative. The total amount of this material from the mother liquors was dissolved in ether, freed from some tarry decomposition products by means of ammonium carbonate solution, and then extracted by shaking with successive portions of a solution of sodium carbonate, when a number of fractions were obtained. Most of these fractions contained some of the sodium compound of homoeriodictyol, which was removed by filtration. The filtrate from the first fraction was discarded, for it was dark green, and, on acidification, yielded only resinous matter, but all the subsequent alkaline, aqueous liquids possessed a clear dark orange colour. They were therefore mixed, acidified, and extracted with ether.

The ethereal solution thus obtained would contain the whole of the high-melting, yellow, phenolic substance, which was previously isolated in small amount by Power and Tutin (*loc. cit.*), and it also gave evidence of containing some eriodictyol. Moreover, in the original investigation by the above-mentioned authors, indications were obtained of the presence of a third compound, crystallising in yellow needles which melted at about 255°. In order, therefore, to render possible the isolation of the constituents of this mixture, advantage was taken of the fact that, in all probability, the several components would vary in their respective affinities for alkali. The material dissolved in the ether was therefore systematically extracted, in fractions, by thoroughly shaking the ethereal solution with thirty-four successive portions of a 5 per cent. solution of sodium carbonate. For each of the first fifteen extractions, 20 c.c. of the solution were employed, and for each of the next ten extractions, 50 c.c., the remaining extractions being accomplished with 100 c.c. each. In every case the alkaline solution was acidified immedately after separation from the ether.

The first and last fractions obtained yielded only resinous matter, but the remainder all contained crystalline products, although each of them also contained some resin. Fractions 2 to 13 inclusive yielded a substance, designated *xanthoeridol*, which formed yellow needles, melting at 258°. Eriodictyol was obtained from fractions 4 to 26 inclusive, and this compound was by far the largest constituent of the mixture. *Chrysoeriol*, the yellow substance previously obtained in small amount by Power and Tutin, occurred in fractions 15 to 26 inclusive, whilst fractions 27 to 33 inclusive yielded a fourth compound, *eriodonol*, which melts at 209°.

Xanthoeridol, $C_{18}H_{11}O_4(OH)_3$.

Fractions 2 to 13 inclusive, above referred to, yielded a product (1·6 grams) which crystallised from a mixture of ethyl acetate and alcohol in tufts of soft, yellow needles melting at 258°:

0·1146 gave 0·2643 CO_2 and 0·0441 H_2O. C = 62·9; H = 4·3.

$C_{18}H_{14}O_7$ requires C = 63·1; H = 4·1 per cent.

The properties of this substance do not agree with those of any compound of the formula $C_{18}H_{14}O_7$ which has previously been described. It is proposed, therefore, to designate it *xanthoeridol*.

Xanthoeridol dissolves in alkalis and in concentrated sulphuric acid, giving a bright yellow colour, and its solution in dilute alcohol is rendered dark brown by ferric chloride.

Triacetylxanthoeridol, $C_{18}H_{11}O_7(CO\cdot CH_3)_3$.—A small quantity of xanthoeridol was boiled for thirty minutes with an excess of acetic anhydride, the greater part of the latter was then removed, and the residue diluted with ether. *Triacetylxanthoeridol* then separates in tufts of slightly yellow needles, which melt at about 169°. After recrystallisation from acetic anhydride, the melting point was raised to 175—176°:

0·1082 gave 0·2443 CO_2 and 0·0441 H_2O. C = 61·6; H = 4·5.
$C_{24}H_{20}O_{10}$ requires C = 61·5; H = 4·3 per cent.

Chrysoeriol, $C_{16}H_9O_3(OH)_3$.

In the first part of this work (*loc. cit.*, p. 367) Power and Tutin described the isolation of a small amount (0·3 gram) of a new, yellow, crystalline substance of phenolic nature, possessing the formula $C_{16}H_{12}O_6$. As so small an amount of this compound was obtained, no name was then given to it. The present authors, however, having now obtained it in larger amount (0·8 gram), and fully confirmed the formula and properties previously assigned to it, propose to designate it *chrysoeriol*.

Chrysoeriol is very sparingly soluble in alcohol, and hence was easily separated from the eriodictyol with which it was associated. On allowing its solution in boiling alcohol to evaporate, it separates in feathery leaflets possessing a golden-yellow colour. It does not melt when heated to 337°:

0·0873 gave 0·2050 CO_2 and 0·0328 H_2O. C = 64·0; H = 4·2.
$C_{16}H_{12}O_6$ requires C = 64·0; H = 4·0 per cent.

Chrysoeriol yields colour reactions which are similar to those of xanthoeridol.

Triacetylchrysoeriol, $C_{16}H_9O_6(CO\cdot CH_3)_3$.—A small quantity of chrysoeriol was boiled for thirty minutes with an excess of acetic anhydride. The anhydride was then decomposed with water, and the resulting solid collected. On crystallisation from a mixture of ethyl acetate and alcohol, the *acetyl* derivative separated in tufts of almost colourless needles, which melted at 200°. After one recrystallisation from ordinary alcohol, the melting point was 196—199°, and, after being boiled for two hours with dilute alcohol, the substance melted indefinitely from 168—178°. This behaviour is evidently due to the fact that triacetylchrysoeriol readily undergoes partial hydrolysis when heated with solvents containing water. When crystallised from acetic anhydride, it melted at 211—212°:

0·0987 gave 0·2244 CO_2 and 0·0393 H_2O. C = 62·0 ; H = 4·4.

$C_{22}H_{18}O_9$ requires C = 62·0 ; H = 4·2 per cent.

Eriodonol, $C_{19}H_{14}O_3(OH)_4$.

The last fractions of material obtained by the above-described fractional extraction with sodium carbonate solution contained a considerable proportion of green, resinous matter, together with a substance which slowly crystallised from slightly diluted alcohol in long, flattened needles, possessing a pale yellow colour. After drying in the air, this compound melted at about 199°, but, after drying at 110° for a short time, fusion occurred at 209°. The total amount obtained was 1 gram :

0·3779, on drying at 110°, lost 0·0174 H_2O. H_2O = 4·6.

0·1245 of anhydrous substance gave 0·2907 CO_2 and 0·0561 H_2O. C = 63·7 ; H = 5·0.

$C_{19}H_{18}O_7,H_2O$ requires H_2O = 4·8 per cent.

$C_{19}H_{18}O_7$ requires C = 63·7 ; H = 5·0 per cent.

In order further to confirm the formula of this compound, a molecular-weight determination was made :

0·2400 in 30 of acetic acid gave Δ^t – 0·090°. M.W. = 351.

$C_{19}H_{18}O_7$ requires M.W. = 358.

This compound, as previously stated (p. 82), is not identical with any substance hitherto described, and the name *eriodonol* is suggested for it. Eriodonol is very readily soluble in ethyl acetate, and dissolves readily in absolute ethyl and methyl alcohols, separating from the last-named solvents in tufts of small needles which are practically anhydrous.

When treated with concentrated sulphuric acid, crystals of eriodonol first become orange-coloured, and then dissolve, giving a yellow solution which exhibits a slight fluorescence. Eriodonol yields with ferric chloride a dark purplish-brown colour, and dissolves in alkalis, giving a not very readily soluble sodium derivative, the solution of which is bright yellow. The tinctorial properties of eriodonol are similar to those of the tetramethyl ether of quercetin described by Kostanecki, Lampe, and Tambor (*loc. cit.*), namely, it dyes linen mordanted with alumina or iron, bright yellow or dark brown respectively. Eriodonol yields iodoform when warmed with iodine and sodium carbonate solution, differing in this respect from xanthoeridol and chrysoeriol.

Tetra-acetyleriodonol, $C_{19}H_{14}O_7(CO\cdot CH_3)_4$.—A small amount of eriodonol was acetylated by boiling with an excess of acetic anhydride, but the resulting *acetyl* derivative crystallised only with difficulty. It was practically insoluble in cold alcohol, being deposited as an oil on allowing its solution in this solvent to cool. It is most conveniently crystallised by concentrating its solution in acetic anhydride to a small bulk, diluting this with ether, and then adding light petroleum. On allowing the mixture to stand for a few days, the acetyl derivative separates in tufts of colourless needles, which melt at 131°:

0·1052 gave 0·2370 CO_2 and 0·0451 H_2O. C = 61·5; H = 4·8.

$C_{27}H_{26}O_{11}$ requires C = 61·6; H = 4·9 per cent.

It is thus apparent that eriodonol contains four hydroxyl groups, but, as its acidic properties are so slight, it is probable that not more than one of them is phenolic.

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XII.—*The Slow Decomposition of Ammonium Chromate, Dichromate, and Trichromate by Heat.*

By Walter Craven Ball.

When ammonium dichromate is heated at temperatures ranging from about 118° to 205°, instead of a sudden decomposition mainly to chromium sesquioxide, nitrogen, and water, such as occurs at higher temperatures, a slow change takes place accompanied with the evolution of ammonia, and a black substance remains. This decomposition has been previously noticed by E. Maumené (*Bull. Soc. chim.*, 1892, [iii], **7**, 174), who found that the salt decomposed slowly at 204°, giving rise ultimately to chromium dioxide.

The author has examined this slow decomposition of the chromates of ammonium (for the trichromate and chromate undergo similar changes), and found, some two years ago, that the final product in the case of the dichromate was a hydrated chromium dioxide, and that ammonia was evolved continuously during the decomposition.

The exact composition of the final product is dealt with in this paper, and has also lately been determined by W. M. Hooton (Proc., 1908, **24**, 27), whose conclusions agree with those of the author, except as to the degree of hydration of the substance. The composition of this end-product does not, however, throw much light on the course of the reaction, as some of the oxygen it contains is absorbed from the air during the heating.

Examination of the Residue obtained by Heating Ammonium Dichromate in Air at 192°.—Weighed amounts of pure finely-powdered ammonium dichromate, dried at 100°, were heated in a V. Meyer bath, various liquids being used as heating agents. At 182° (boiling aniline) the decomposition was very slow, whilst at 205° (boiling nitrobenzene) the rate of decomposition was much increased, but sooner or later the ordinary deflagration to chromium sesquioxide, nitrogen, and water took place. At 192° the slow decomposition occurred with sufficient rapidity, and the explosive decomposition did not supervene.

At this temperature the darkening of the salt was observable within a few minutes, and after two hours' heating the substance had become quite black. When large crystals were used instead of the finely divided powder, it was evident that decomposition had begun at the surface, leaving unaltered dichromate beneath.

The heating was continued for several days, until the product had reached an approximately constant weight. The weight decreased steadily at first, and then increased slightly. The residue was a black, amorphous, hygroscopic powder, slowly acted on by water, yielding chromic acid and hydrated chromium sesquioxide, and rapidly by alkalis, yielding the hydrated sesquioxide and a chromate. It did not contain nitrogen.

Six distinct samples were analysed, the results being given in table I. The active oxygen was in some cases determined iodometrically; in others, by decomposing with alkali and estimating the resulting chromate with ferrous salts. The sesquioxide was determined by ignition, and the water by direct weighing.

TABLE I.

No.	Cr_2O_3 per cent.	Active oxygen per cent.	H_2O per cent.
1	84·42	8·98	6·74
2	84·06 ; 83·63	9·08	6·86
3	83·06 ; 83·02	9·18 ; 8·97 ; 9·01	6·54 ; 6·56
4	84·10 ; 84·41	8·88 ; 8·84	7·03 ; 7·22
5	—	9·02	7·50
6	84·45	—	—

$3CrO_2,H_2O$ requires $Cr_2O_3 = 84·46$. O (active) = 8·88 ; $H_2O = 6·66$ per cent.

$2CrO_2,H_2O$ requires $Cr_2O_3 = 81·74$. O (active) = 8·59 ; $H_2O = 9·67$ per cent.

The numbers thus agree fairly well with those required by the formula $3CrO_2,H_2O$, and differ considerably from those required by the formula $2CrO_2,H_2O$. The variations between the different samples are, however, larger than might be expected for a perfectly definite substance.

In order to eliminate oxidation by the air, and to discover, if possible, the intermediate stages of the decomposition, the dichromate, trichromate, and the chromate were each heated in a stream of nitrogen at constant temperatures.

In each case the course of the decomposition was similar ; nitrogen, ammonia, and water were evolved, and the salt rapidly became black. From this black substance, water extracted some unchanged salt, leaving an amorphous, insoluble, black residue, which yielded, on hydrolysis with alkali hydroxide, chromate, chromic hydroxide, and ammonia.

Three experiments (*A*, *B*, and *C*) were made with ammonium dichromate ; in *A*, the salt was heated for four and a-half hours at an average temperature of 195·2° ; *B* was similar, except that the average temperature, 193·8°, was slightly lower, and *C* was made in nitrogen under about 20 mm. pressure. In this case the apparatus was altered slightly, the water and ammonia evolved being collected together in concentrated sulphuric acid, and the ammonia alone estimated.

Experiment *D* was made with the trichromate, $(NH_4)_2Cr_3O_{10}$, and *E* with the chromate, $(NH_4)_2CrO_4$; in detail they were similar to experiments *A* and *B*.

As the methods of estimation used in each case were similar, they are given below, in the account of the experiments with the dichromate. The black insoluble residues obtained after extraction with water of all unchanged salt from the product of each experiment were very similar in appearance and properties. Their compositions are given in table IV (p. 92).

Method of Heating.—The heating apparatus consisted of a large corked boiling tube containing methyl benzoate ; through the cork passed a condenser and a test-tube. The latter was closed by an indiarubber stopper, through which passed a thermometer, the tube leading in the nitrogen, and that conducting out the water, nitrogen, and ammonia evolved. Inside this test-tube was placed a weighed quantity of the finely-powdered dichromate, contained in a short, wide tube provided with a loop of platinum wire, so that it could easily be removed from the heating apparatus.

The water evolved was collected in a U-tube containing solid potassium hydroxide, and, after its removal, the stream of nitrogen containing the evolved ammonia was led into a three-necked flask containing *N*/10-acid tinted with methyl-orange. The jet of a burette passed through one of the necks, so that a measured amount of acid could be added at any time. By this arrangement, the amount of ammonia evolved at any stage could be found, and, at the end of the experiment, the weight of water formed and the loss in weight of the dichromate also, giving, by difference, the weight of nitrogen evolved from the dichromate. As the amounts of ammonia evolved were small, a blank experiment was first made, proving that the apparatus was entirely free from ammonia.

The nitrogen used was prepared by dropping a concentrated solution of pure sodium nitrite into a slightly warmed solution of ammonium chloride, and purified by passing through wash-bottles containing ferrous sulphate solution, concentrated aqueous sodium hydroxide, concentrated sulphuric acid, and through two tubes containing red-hot copper. When an experiment was to be made, the nitrogen was driven from the gas-holder through a wash-bottle containing concentrated sulphuric acid, through a potash tower, and thence into the heating apparatus by means of a delivery tube, which came within 1 cm. of the surface of the dichromate, so that the products evolved should be removed as quickly as possible.

After each experiment, the black solid resulting from the decomposition of the salt was treated with water several times until practically nothing more was dissolved from it. Although water had a slight action on the insoluble part, it was not difficult to discover when all the soluble portion (proved to be unaltered ammonium dichromate by estimations of chromic acid and ammonia) had been extracted. For instance, in experiment *B*, extraction with water at the ordinary temperature for fifteen minutes withdrew 1·5912 grams of unaltered dichromate, whereas a further extraction, for the same length of time, removed an amount estimated to be not more than one milligram.

The insoluble portion, that is, the residue left by the dichromate that had undergone decomposition, was separated from the extracted unaltered salt by filtration in a Gooch crucible, and was then decomposed by boiling with sodium hydroxide in a current of steam, the evolved ammonia being determined by standard acid.

The other products of the action of sodium hydroxide, namely,

TABLE II.

Expt.	Time of heating in hours.	Temp.	Weight taken.	Weight decomposed.	Loss in weight.	Water evolved.	Ammonia evolved.	Nitrogen (by diff.).
A	4½	195·2°	3·2653	1·6376	0·3139	0·2135	0·0185	0·0819*
B	4½	193·8	2·3393	0·7481	0·1316	0·0832	0·0074	—
C	2½	195·0	1·4418	0·7410	0·1305	—	0·0109	—
D	3	194·7	3·4862	1·2776	0·1733	0·1179	0·0031	—
E	3	195·8	1·7270	all	0·5564	0·2721	0·1923	—

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* The accuracy of this amount of nitrogen, obtained by difference, may be verified thus:

Total nitrogen originally present in 1·6376 grams of dichromate (this being the amount of the salt decomposed) $=0·1818$ gram.

Nitrogen found in residue from this dichromate $=0·0839$ gram.

Nitrogen evolved as $NH_3=0·0152$ gram: therefore nitrogen evolved in free state $=0·1818-(0·0839+0·0152)=0·0827$ gram, a value which is in close agreement with the amount, 0·0819 gram, found as above.

sodium chromate and chromic hydroxide, were then separated by filtration, and the chromate determined by ferrous iron.

Details of each experiment are given in tables II and III; table IV contains the analyses of the insoluble residues.

The following numbers, representing c.c. of acid ($N/10 \times 1{\cdot}055$) neutralised by the evolved ammonia in expt. *A*, show that it was evolved at a constant rate.

In first hour, 2·06; in second hour, 2·48; in third hour, 2·50; and in fourth hour, 2·33.

TABLE III.

Expt.	Amount of decomposition of salt per 100 grams per hour.	Rate of evolution of NH_3 per 100 grams of salt per hour.	Ratio. $\frac{\text{Nitrogen evolved in free state.}}{\text{Nitrogen evolved as } NH_3\text{.}}$
A	11·15 grams.	0·126 gram.	5·4
B	7·11 ,,	0·070 ,,	5·7
C	19·44 ,,	0·250 ,,	4·2
D	12·22 ,,	0·030 ,,	20·8
E	—	—	**0·56**

From the figures given, it may be seen that rise of temperature and lowering of pressure have considerable effect in increasing the rate of decomposition of the dichromate, yet do not much influence the fraction of the contained nitrogen evolved as ammonia.

The rate of decomposition of the trichromate was greater than that of the dichromate, but, as might have been anticipated, much less of its nitrogen was evolved as ammonia.

In experiment *E*, on extracting the solid product of the decomposition with water, it was found that 98 per cent. of the chromate had been transformed into a black, insoluble residue, whilst 2 per cent. dissolved as ammonium dichromate.

It seemed probable that the ammonium chromate would be very rapidly decomposed into the dichromate, ammonia, and water according to the equation:

$$2(NH_4)_2CrO_4 = (NH_4)_2Cr_2O_7 + 2NH_3 + H_2O,$$

as this decomposition occurs slowly at the ordinary temperature and rapidly at 100°. After this supposed conversion into dichromate had taken place, the rest of the decomposition might be expected to be identical with that of the dichromate. This was partly confirmed by experiment, for it was found that the ammonia evolved during the first twenty-five minutes' heating neutralised 92·5 c.c. of acid; during the second twenty-five minutes, 13·0 c.c. of acid, and during the third twenty-five minutes, 1·8 c.c. of acid.

Thus, of the total amount of ammonia, 0·3860 gram, contained in the chromate used, 0·1923 gram, or almost exactly half, was evolved as ammonia, and more than nine-tenths of this evolution took place during the first thirty minutes' heating.

The dichromate formed from the chromate, however, decomposed much more rapidly than the dichromate used in experiments *A*, *B*, and *C*. For example, in experiment *A*, after four and a-half hours' heating, only half of the salt had been transformed into the insoluble residue, whilst, in this case, three hours' heating at almost the same temperature had decomposed practically the whole of the salt.

It will be seen, also, in table IV that, although the dichromate and chromate residues were similar in properties, the chromate residue contained considerably more chromium sesquioxide,

Examination of the Insoluble Residues.—The solid residues, obtained by the decomposition of the salts in the foregoing experiments, were all black, amorphous solids, very similar in appearance. They were insoluble in water, but were slowly acted on by it to a slight extent, giving up chromium trioxide and ammonia. The residue from the trichromate was the most easily acted on by water, but the difference was not great. All were decomposed similarly, by boiling with aqueous sodium hydroxide, into sodium chromate, chromic hydroxide, and ammonia.

Experiments proved that these residues took up small amounts of water during the extraction of the unchanged salts, but in table IV the percentage compositions are those of the residues before this absorption of water had taken place.

TABLE IV.

	Composition in percentages of substances formed on hydrolysis.				Composition expressed in molecular ratios.			
Expt.	Cr_2O_3.	CrO_3.	NH_3.	H_2O.	Cr_2O_3.	CrO_3.	NH_3.	H_2O.
A	34·85	52·36	7·70	5·09	1·00	2·29	1·98	1·24
B	32·51	53·58	8·26	5·66	1·00	2·51	2·28	1·47
C	32·76	53·27	7·11	6·86	1·00	2·47	1·94	1·77
D	31·72	56·87	5·31	6·10	1·00	2·73	1·50	1·63
E	39·08	46·12	7·12	7·70	1·00	1·79	1·63	1·67

As stated above, these residues were slightly acted on by water, and consequently, in separating them from the unchanged salts, a very small amount of decomposition took place, but this was not sufficient materially to alter their compositions.

It will be seen that the dichromate residues do not differ much from one another in composition; in particular, those from experiments *B* and *C* have almost identical percentages of chromium sesquioxide and chromium trioxide, although these experiments were made under different conditions; these two residues likewise contain chromium sesquioxide, chromium trioxide, and ammonia in molecular ratios which approach to simple whole numbers (2 : 5 : 4). The properties of these residues are not those of ammonium salts in general, for they are black, insoluble, and amorphous ; the production from them, on hydrolysis, of a chromate and ammonia may indicate possibly that they are mixtures of chromium sesquioxide, formed by the reduction of the chromium trioxide of the salts by the hydrogen of the ammonium radicle, with some substance, such as an amide, capable of yielding chromic acid and ammonia on hydrolysis, and produced by a simultaneous dehydration of the salt.

The evolution of ammonia at a uniform rate throughout the decomposition of the dichromate renders it unlikely that it is a secondary product formed, for instance, by the action of the basic sesquioxide produced by decomposition of part of the salt on the undecomposed portion.

A few experiments were also made in order to estimate the amount of ammonia evolved in the ordinary rapid decomposition of the dichromate, but the exact estimation was rendered difficult owing to the simultaneous production of oxides of nitrogen. In the experiments made, the nitrogen evolved as ammonia was always in excess of that evolved in the form of oxides.

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XIII.—*The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part III.*

By ARTHUR SLATOR and DOUGLAS FRANK TWISS.

IN two previous communications by one of us (Trans., 1904, **85**, 1286 ; 1905, **87**, 482), some account has been given of measurements of the velocity of the reactions between sodium thiosulphate and a number of organic halogen compounds. The reaction consists in the replacement of the halogen by the group NaS_2O_3, and proceeds quantitatively in dilute solution in the case of a large number of organic compounds.

The velocity of these reactions (except with two dihalogen compounds) is approximately proportional to the concentration of the sodium thiosulphate. From a consideration of the rates of reaction of a number of metallic thiosulphates with ethyl bromoacetate, it is concluded that the reaction is one primarily connected with the S_2O_3''

ion, and that such complex ions as AgS_2O_3', $Ag(S_2O_3)_2'''$, and $Pb(S_2O_3)_2''$ are relatively inert.

The velocity of the reaction is also proportional to the concentration of the halide, and sodium thiosulphate can therefore be used as a reagent to compare the activities of a number of such compounds.

The present communication contains an account of the reactions with other types of halogen compounds. Sodium thiosulphate reacts with propyl iodide, forming sodium propyl thiosulphate, and analogous compounds are also obtained when the reaction is carried out with *iso*propyl iodide and with allyl iodide (Purgotti, *Gazzetta*, 1892, **22**, i, 416).

In dilute solution, *n*-propyl and allyl iodides react quantitatively, as shown by the following experiments. Weighed quantities of the iodides were allowed to react with excess of sodium thiosulphate in aqueous-alcoholic solution, and the excess of thiosulphate titrated after completion of the reaction :

0·0950 gram n-C_3H_7I required 53·1 c.c. $N/100$-$Na_2S_2O_8 =$
$C_3H_7I : 0{\cdot}95Na_2S_2O_3$.
0·0950 gram n-C_3H_7I required 52·6 c.c. $N/100$-$Na_2S_2O_8 =$
$C_3H_7I : 0{\cdot}94Na_2S_2O_3$.
0·3710 gram C_3H_5I required 21·6 c.c. $N/10$-$Na_2S_2O_3 =$
$C_3H_5I : 0{\cdot}98Na_2S_2O_3$.

In the case of *iso*propyl iodide the reaction proceeds too slowly to measure this ratio.

Velocity experiments were carried out, using as a solvent a mixture of alcohol and water in the proportion of five to three by volume. Solutions of the two reagents in suitable concentration were mixed, and the reaction followed by titration with $N/100$-iodine solution in the manner previously described. The experiments were carried out in flasks resting in a thermostat.

The constant K is calculated by the usual formula for a bimolecular reaction: $K \times C_\infty = \frac{I}{t} \log. C_oC_t'/C_o'C^{t}$

where $t =$ time in minutes ;
$C_o, C_o' =$ the initial concentrations of the two reagents ;
$C_t, C_t' =$ the concentrations after time t ;
$C_\infty =$ the concentration of the excess of sodium thiosulphate expressed in gram-equivalents per litre.

The infinity value of the sodium thiosulphate titre is the final constant value obtained when the reaction is complete. In the case of *iso*propyl iodide, the reaction proceeds too slowly to obtain this value experimentally, and it is calculated on the assumption that the reagents react in equivalent proportions. The tables show that *n*-propyl iodide is nearly seventeen times as reactive as *iso*propyl iodide, whilst allyl iodide is 173 times as reactive as *n*-propyl iodide. The activity of allyl iodide is remarkable, as it is even more reactive than methyl iodide.

Details of the titrations are given in the case of the reaction with allyl iodide in order to show the method of calculation and the typical agreement of the results. In the case of the other reactions, only the initial and final values of the thiosulphate titrations and the mean value of the velocity constant K are given.

TABLE I.—*Allyl and Propyl Iodides.*

Solvent.—Alcohol + water (5 : 3 by vol.).

Allyl Iodide.

Temperature, 25°.

10 c.c. titrated. I = 0·0124 *N*.

Time.	($Na_2S_2O_3$).	(C_3H_5I).	$K \times C_\infty$.
0	16·58	7·26	—
2½	14·07	4·75	0·045
6	12·36	3·04	0·042
10	11·10	1·78	0·044
20	9·99	0·67	0·041
∞	9·32	0	—
		Mean.........	0·043

$K = 3·7$.

Another expt. gave $K = 3·6$.
Mean.. ...... $K = 3·65$.

Allyl Iodide.

Temperature, 15°.

5 c.c. titrated. I = 0·00992 *N*.

Time.	($Na_2S_2O_3$).	(C_3H_5I).	$K \times C_\infty$.
0	20·34	7·05	—
3	18·11	4·82	0·038
7	16·40	3·11	0·0375
12	15·14	1·85	0·038
20	14·17	0·88	0·0375
∞	13·29	0	—
		Mean.........	0·038

$K = 1·44$.

Other expts. gave $K = 1·43$, 1·32, 1·34.
Mean ..... $K = 1·38$.

Temperature quotient = 2·65.
Calculated value at 35°: $K = 9·7$.

n-*Propyl Iodide*: 2 c.c. titrated.

Temperature.	Solvent.	Extreme values ($Na_2S_2O_3$).	K.
35°	Alcohol + water	18·1 c.c.—11·8 c.c.	0·054
,,	,,	14·9 c.c.— 8·9 c.c.	0·058
,,	,,	17·9 c.c.—11·8 c.c.	0·056
		Mean...............	0·056

iso*Propyl Iodide*: 2 c.c. titrated.

35°	Alcohol + water	20·2 c.c.—10·3 c.c.	0·0034

Chloroacetone and chloroacetophenone react very rapidly with sodium thiosulphate, and, as the following experiments show, the interaction takes place quantitatively:

0·1315 gram C_3H_5OCl required 13·9 c.c. $N/10$-$Na_2S_2O_3$ =
$C_3H_5OCl : 0·98Na_2S_2O_3$.

0·1425 gram C_8H_7OCl required 9·3 c.c. $N/10$-$Na_2S_2O_3$ =
$C_8H_7OCl : 0·99Na_2S_2O_3$.

Velocity measurements of the reaction with chloroacetone were carried out in aqueous solution and also in aqueous-alcoholic solution. The reaction with chloroacetophenone could be carried out only in aqueous alcohol. As the following tables show, these chlorides are very reactive. They are more reactive than any other chloride used in this series of investigations. The corresponding bromine compounds react almost instantaneously under these conditions, and no measurements of the velocity of the reactions were obtained.

Chloroacetone is six times as reactive as ethyl chloroacetate, and seventeen times as reactive as methyl chloride.

The compounds formed by these reactions are easily isolated, but a description of them is reserved for a future communication, when it is hoped also to describe other derivatives.

TABLE II.—*Chloroacetone and Chloroacetophenone.*

Chloroacetone.

Temperature.	Solvent.	Vol. titrated.	Extreme values ($Na_2S_2O_3$).	*K*.
25°	Water	10 c.c.	28·9 c.c.—16·6 c.c.	0·38
,,	,,	,,	29·2 c.c.—16·5 c.c.	0·37
,,	,,	,,	27·4 c.c.—13·1 c.c.	0·385
,,	,,	,,	31·2 c.c.—14·9 c.c.	0·365
			Mean...............	0·375
15°	,,	,,	25·2 c.c.—11·6 c.c.	0·133
,,	,,	,,	26·4 c.c.—10·4 c.c.	0·134
			Mean...............	0·134

Temperature quotient = 2·8.

15°	Alcohol + water	5 c.c.	20·7 c.c.—9·9 c.c.	0·57

Chloroacetophenone.

15°	Alcohol + water	5 c.c.	20·1 c.c.—11·7 c.c.	0·64
,,	,,	,,	27·4 c.c.—15·6 c.c.	0·66
			Mean........... ...	0·65

Benzyl chloride and sodium thiosulphate react, forming sodium benzyl thiosulphate. A specimen of the isolated salt gave on analysis:

0·3020 gave 0·0940 Na_2SO_4. Na = 10·09.
0·2840 ,, 0·0895 Na_2SO_4. Na = 10·22.
$C_7H_7O_3S_2Na$ requires Na = 10·18 per cent.

o-, *p*-, and *m*-Nitrobenzyl chlorides form the corresponding salts (Price and Twiss, Trans., 1908, **93**, 1401). The four chlorides react quantitatively with sodium thiosulphate:

0·3495 gram C_7H_7l required 26· c.c. $N/10\text{-}Na_2S_2O_3 = C_7H_7Cl : 0{\cdot}96Na_2S_2O_3$.

0·3225 gram o-$C_7H_6O_2NCl$ required 18·8 c.c. $N/10$-$Na_2S_2O_3$ = $C_7H_6O_2NCl : 1·00Na_2S_2O_3$.

0·3068 gram p-$C_7H_6O_2NCl$ required 17·6 c.c. $N/10$-$Na_2S_2O_3$ = $C_7H_6O_2NCl : 0·98Na_2S_2O_3$.

0·3830 gram m-$C_7H_6O_2NCl$ required 22·3 c.c. $N/10$-$Na_2S_2O_3$ = $C_7H_6O_2NCl : 1·00Na_2S_2O_3$.

Measurements of the velocity of these reactions were carried out at 35° in aqueous-alcoholic solution. The following table shows that the velocities of reaction with benzyl chloride and with *o*-nitrobenzyl chloride are approximately equal. *p*-Nitrobenzyl chloride is about twice as reactive as these two compounds, and the activity of the meta-compound lies between that of the ortho- and the para-derivative. The activity of these compounds is of the same order as that of methyl chloride.

TABLE III.—*Benzyl Chloride and the Nitrobenzyl Chlorides.*

Solvent.—Alcohol + water (5 : 3 by vol.).

Temperature 35° : 2 c.c. titrated.

	Extreme values, $Na_2S_2O_3$.	K.
Benzyl chloride	17·0 c.c.—8·5 c.c.	0·169
,,	17·9 c.c.—8·5 c.c.	0·162
	Mean	0·166
o-Nitrobenzyl chloride	17·2 c.c.—10 9 c.c.	0·162
,,	14 5 c.c. — 9·8 c.c.	0·170
	Mean	0·166
p-Nitrobenzyl chloride	19 5 c.c.—12·6 c.c.	0·297
,,	13·7 c.c.—10·4 c.c.	0·312
	Mean	0·305
m-Nitrobenzyl chloride	16·5 c.c.—11·4 c.c.	0·192
,,	17·7 c.c.—12·2 c.c.	0·194
,,	19·6 c.c.—14·3 c.c.	0·196
	Mean	0·194

Ethyl α-bromopropionate and ethyl α-bromobutyrate interact with one equivalent of sodium thiosulphate :

0·4863 gram $C_5H_9O_2Br$ required 25·1 c.c. $N/10$-$Na_2S_2O_3$ = $C_5H_9O_2Br : 0·93Na_2S_2O_3$.

0·4883 gram $C_5H_9O_2Br$ required 25·2 c.c. $N/10$-$Na_2S_2O_3$ = $C_5H_9O_2Br : 0·93Na_2S_2O_3$.

0·5062 gram $C_6H_{11}O_2Br$ required 24·9 c.c. $N/10$-$Na_2S_2O_3$ = $C_6H_{11}O_2Br : 0·96Na_2S_2O_3$.

0·666 gram $C_6H_{11}O_2Br$ required 32·6 c.c. $N/10$-$Na_2S_2O_3$ = $C_6H_{11}O_2Br : 0·95Na_2S_2O_3$.

The reactions proceed with measurable velocity at 25° and 35°. Aqueous alcohol was used as the solvent.

TABLE IV.—*Ethyl a-Bromopropionate.*

Solvent.—Alcohol + water (5 : 3 by vol.)

2 c.c. titrated.

Temperature.	Extreme values of ($Na_2S_2O_3$).	*K*.
35°	17·3 c.c.— 8·3 c.c.	0·085
25	20·4 c.c.—11·5 c.c.	0·037

Temperature quotient = 2·3.

Ethyl a Bromobutyrate.

35°	21·1 c.c.—12·6 c.c.	0·022

The values of *K* in these two experiments depend to some extent on the initial concentration of the reagents. More dilute solutions were found to give higher values of the velocity constant.

Ethyl chloropropionate, ethyl bromo*iso*butyrate, and ethyl bromo*iso*valerate react too slowly to give satisfactory measurements.

Trimethylene dibromide reacts with sodium thiosulphate with an approximate velocity $K = 0·02$ in aqueous-alcoholic solution at 35°. Both bromine atoms are apparently replaced, but the reaction has not been further investigated.

Trimethylene chlorobromide reacts slowly, and propylene dibromide still more slowly. Epichlorohydrin and ethyl chlorocarbonate react comparatively rapidly with sodium thiosulphate, but the reactions are complicated by the simultaneous hydrolytic replacement of the chlorine. The following approximate values of the velocities were obtained :

Epichlorohydrin, $K = 0·1$ at 35°.
Ethyl chlorocarbonate, $K = 1·0$,, 35°.

Ethylene chlorohydrin reacts with sodium thiosulphate, but too slowly for exact measurement. Chloroacetal does not react, or reacts only very slowly with thiosulphates.

With the following compounds no reaction with sodium thiosulphate could be detected: iodobenzene, bromobenzene, *o*-bromotoluene, *p*-bromotoluene, *o*- and *m*-chloronitrobenzenes, and benzylidene chloride.

Picryl chloride and sodium thiosulphate interact comparatively rapidly, with formation of a compound which crystallises out during the reaction. The reaction is being further investigated. Acid chlorides react with sodium thiosulphate, but the reaction is complicated by hydrolysis of the acid chloride.

The velocity constants obtained in this and in the previous communications can be conveniently summarised in the following table.

TABLE V.—*Summary of Velocity Constants.*

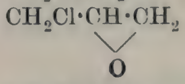
Solvent.—Water.

	15°.	25°.	35°.	50°.	Temperature quotient for 10°.
Methyl iodide...	0·280	0·85			3·05
,, bromide	0·29	0·91			3·1
,, chloride	0·0066	0·022	0·068		3·2
Ethyl iodide		0·050	0·170		3·4
,, bromide		0·031		0·50	3·0
Ethylene bromide				0·049	2·9
Ethyl iodoacetate	2·55	7·0			2·75
,, bromoacetate	2·36	6·4			2·75
,, chloroacetate		0·060	0·173		2·9
Methyl bromoacetate	2·09	5·85			2·8
,, chloroacetate		0·059	0·165		2·8
Sodium bromoacetate		0·31	0·67	1·95	2·1
,, chloroacetate		0·0042		0·0395	2·45
Chloroacetone	0·134	0·375			2·8
Solvent.—Alcohol + water (5 : 2 by vol.).					
Methyl iodide	0·80				
Ethylene iodide	0·17*	0·50*			2·9
,, bromoiodide	0·105*	0·275*			2·6
Solvent.—Alcohol + water (5 : 3 by vol.).					
Propyl iodide			0·056		
*iso*Propyl iodide			0·0034		
Allyl iodide	1·38	3·65			2·65
Bromoacetone	large				
Chloroacetone	0·57				
Bromoacetophenone	large				
Chloroacetophenone	0·65				
Ethyl α-bromopropionate		0·037	0·085		2·3
,, α-bromobutyrate			0·022		
,, α-bromo*iso*butyrate			small		
Benzyl chloride			0·166		
o-Nitrobenzyl chloride			0·166		
p-Nitrobenzyl chloride			0·305		
m-Nitrobenzyl chloride			0·194		
Ethyl chlorocarbonate			1·0		
Epichlorohydrin			0·1		
Ethylene chlorohydrin			small		
Trimethylene dibromide			0·01*		
Propylene dibromide			small		
Chloroacetal			small		

* In these cases, two halogen atoms are replaced, and the velocity coefficients have therefore been halved.

A consideration of this table of results shows that various substituents greatly alter the activity of the methyl halides towards sodium thiosulphate. Bromoacetone and bromoacetophenone are the most reactive compounds that have been investigated. The esters of the substituted acetates rank next in activity. Ethyl chlorocarbonate also reacts quickly with sodium thiosulphate. All these compounds contain the carboxyl group, to which the great activity can be attributed. An ethylene linking has a similar influence; thus allyl iodide is more reactive than any alkyl iodide. Compounds containing other substituents are in all cases less reactive than the methyl halide, with the exception of some benzyl derivatives. The activity of methyl chloride lies between that of benzyl and *p*-nitrobenzyl chloride. The influence of these benzene substituents is therefore relatively small. The great activity of the allyl and benzyl derivatives is probably due in each case to the unsaturated nature of the compound. The ethyl halides are less reactive than the corresponding methyl compounds, and, as we ascend the alkyl series, the activity rapidly diminishes. The substituted acetates are very reactive, but the activity of the corresponding propionate and butyrate is much less. In each of these two series of compounds the *iso*-derivatives are much less reactive than the corresponding normal compounds.

The group $\cdot CH_2I$ has a less inhibiting effect than the methyl group; thus ethylene di-iodide is less reactive than methyl iodide, but more reactive than ethyl iodide. The $\cdot CH_2Br$ group has a greater inhibiting effect than the methyl group; thus ethylene dibromide is less reactive than ethyl bromide.* Propylene dibromide is less reactive than trimethylene dibromide. The fall in activity of the following series of compounds is interesting:

$CH_2Cl\cdot COMe$	$K = 0{\cdot}375$.
$CH_2Cl\cdot CO_2Me$	$K = 0{\cdot}059$.
 $CH_2Cl\cdot CH\cdot CH_2$ (O)	$K = 0{\cdot}01$ (approximately).
$CH_2Cl\cdot CO_2Na$	$K = 0{\cdot}0042$.
$CH_2Cl\cdot CH_2\cdot OH$	$K =$ small.
$CH_2Cl\cdot CH(OEt)_2$	$K =$ small.

The hydroxyl group and its derivatives evidently have a considerable inhibiting effect on the activity of the compound.

The ratio of activity of chlorides, bromides, and iodides is as follows:

	Iodide.	Bromide.	Chloride.
Methyl	1	1·07	0·026
Ethyl	1	0·62	—
Ethyl halogen acetate	1	0·91	0·009
Methyl halogen acetate	—	1	0·010
Sodium halogen acetate	—	1	0·013

The influence of the solvent on the velocity coefficients is large. Methyl iodide is three times as reactive in aqueous alcohol (5 : 2) as in water. Chloroacetone is about four times as reactive in aqueous alcohol (5 : 3) as in water. These factors have been used to obtain comparative coefficients when experiments were carried out in different solvents. The differences in velocity are in most cases so great that these approximate factors can be used, but many of the measurements which have been carried out in aqueous solution can, with advantage, be repeated, using the composite solvent.

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* In the table, Trans., 1904, **85**, 1304, the number opposite $C_2H_4Br_2$ should read 0·0034 instead of 0·034.

The temperature-coefficients of eighteen of these reactions have been measured, and are given in the table. Definite groups of halides appear to give almost identical temperature-coefficients, but the total variation is too small to draw any general conclusions.

It has been pointed out by Miss K. A. Burke and F. G. Donnan (Trans., 1904, **85**, 55) that the reactions between the alkyl iodides and various reagents can be divided into two groups. To the first belong the reactions with ethyl sodioacetoacetate (Wislicenus), triethylamine (Menschutkin), and sodium ethoxide (Hecht, Conrad, and Brüchner).

The resemblance between them is mainly in certain qualitative relationships in the velocity coefficients of the three sets of reactions. The reactions with sodium thiosulphate can also be classed in this group. This is clearly shown by a comparison of the velocity coefficients of this reaction and the one with ethyl sodioacetate. The order of activity of the iodides is in each case: allyl, methyl, ethyl, propyl, *iso*propyl. The reactions with sodium thiosulphate have been extended to a number of halogen compounds which have not yet been used in the other three cases. Many of the halides which react so rapidly with sodium thiosulphate probably also react rapidly with the other reagents of group 1. It remains to be seen if resemblances can be traced over this wider range of reactions.

The second group of reactions differs in many ways from the first. Burke and Donnan find that if the activities of the alkyl iodides are measured by the velocity coefficients of the reaction with silver nitrate, the order is: *iso*propyl, ethyl, *n*-propyl, methyl, *n*-butyl, *iso*amyl, *iso*butyl.

They draw attention to the difference between this order of activity and that found in the case of the reactions of group 1.

The order of activity corresponds almost completely with that given by the rate of production of free iodine in alcoholic solutions of the iodides when exposed to light and air. Silver nitrate and dissolved oxygen can therefore be classed as reagents of group 2. The oxidation of the iodides is accelerated by the addition of potassium iodide. The decomposition of ethylene di-iodide and ethylene bromoiodide is greatly influenced by the presence of potassium iodide (Slator, Trans., 1904, **85**, 1697), and it is therefore possible that the catalytic decompositions of these ethylene derivatives are reactions closely allied to those of group 2.

Euler (*Ber.*, 1906, **39**, 2726) has described other differences between the two groups of reactions. He shows that when chloroacetic acid, bromoacetic acid, and ethyl bromide react with silver nitrate, the velocity coefficients do not in any way correspond with those measured by the rate of hydrolysis of the halides by sodium hydroxide.

The latter reaction does not belong to those of group 2, and it is doubtful whether it ought to be classed with those of group 1 (Burke and Donnan, *loc. cit.*, p. 560). Euler also finds that sodium chloroacetate is eight times as reactive as ethyl chloroacetate when the reaction with silver nitrate is used to measure the activities. Sodium thiosulphate, on the other hand, reacts fourteen times as rapidly with the ester as with the sodium salt.

Burke and Donnan (*loc. cit.*, p. 558), in discussing the reactions of group 1, conclude that the reactivity of the iodides in the three reactions is due to the same condition or function of the molecule. The reactions of group 2 would seem to be dependent on some other condition of the molecule, for we get resemblances between the two reactions of this group and marked differences between the reactions of the two groups. It is suggested that the two conditions of the molecule are in reality two different forms of the halide, and that one group of reagents acts on one form and the other group on the second form of the halide.

There is no difficulty in constructing equations to represent the equilibrium between the different forms, and at the same time bring them into agreement with the experimental results. The suggestion is further supported by some other results of this investigation.

When sodium thiosulphate reacts with ethylene chloroiodide and with the chlorobromide, the velocity is independent of the concentration of the thiosulphate (Trans., 1904, **85**, 1301).

This admits of easy explanation on the assumption that the active form of the halide reacts rapidly with the sodium thiosulphate. The change measured in this case is the reaction involving the formation of the active form of the halide, and this is a reaction quite independent of the thiosulphate.

We are not yet able to bring forward a plausible suggestion as to the chemical nature of the different forms of the halide, but we can say with some certainty that they are not of the nature of dissociated substances of the electrolytic or "alkylidene" or "alkylene" type suggested by Nef and discussed by other investigators.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the cost of this investigation.

The main part of the experimental work of this research was carried out in the Chemical Laboratories of the Birmingham Municipal Technical School. We desire to acknowledge our indebtness to Dr. T. Slater Price for valuable help given us during the progress of the work.

XIV.—*The Crystallisation of Externally Compensated Mixtures.*

By Frederic Stanley Kipping and William Jackson Pope.

As attention has again been directed by the work of Ostromisslensky (*Ber.*, 1908, **41**, 3035) to the interesting nature of the problems involved in the crystallisation of externally compensated mixtures, we think it desirable to record briefly the results of some experiments on the subject which we commenced in 1898; our joint work was interrupted several years later, before it had been brought to a definite issue, by the cessation of our collaboration.

Eleven portions of a solution of sodium ammonium *d*- and *l*-tartrates, prepared from racemic acid, were nearly saturated with dextrose and then allowed to evaporate spontaneously; one only yielded an optically inactive crop of crystals, whilst the other ten afforded deposits which, after recrystallisation, consisted principally or entirely of sodium ammonium *d*-tartrate. As the racemic acid used in preparing the sodium ammonium salt had been polarimetrically examined and found to be optically inactive, and, as a further precaution, had been subsequently crystallised from water, we concluded that the presence of the dextrose in the solution was responsible for the resolution of the mixture of *d*- and *l*-tartrates; a preliminary note was published embodying these observations (Proc., 1898, **14**, 113).

After confirming these results by repetition and by performing analogous experiments in solutions of lævulose, all of which yielded strongly dextrorotatory deposits of sodium ammonium salt, we carried out similar series of spontaneous crystallisations omitting addition of the sugar. It was then found that when racemic acid, obtained from Kahlbaum, and further purified by crystallisation from water, was converted into its sodium ammonium salt and aqueous solutions of this salt were allowed to evaporate spontaneously in open beakers so that only a few large crystals separated, the deposits consisted wholly or in the main of sodium ammonium *d*-tartrate; when, however, the deposits consisted of numerous small crystals, they were, in general, almost or quite optically inactive.

These observations seemed to suggest that our racemic acid, notwithstanding its apparent optical inactivity, still contained a slight excess of *d*-tartaric acid; it is conceivable that a very minute excess of the *d*-acid could cause the *d*-tartrate to crystallise out before the enantiomorphously related salt, and so give rise to the experimental results described above.

As racemic and tartaric acids differ entirely in crystalline form and in the proportions of water of crystallisation which they take up, and as the former acid is much more soluble in water than the latter, the recrystallised, well-washed racemic acid should be optically inactive, and any *d*-tartaric acid originally present should be found in the mother liquors. Since the examination of such liquors seemed to offer the best mode of detecting *d*-tartaric acid in our purchased samples of racemic acid, a fresh quantity (487 grams) of racemic acid was systematically recrystallised from water; each deposit was well washed by the aid of the pump, and the combined filtrates and washings concentrated. These operations were repeated until the most soluble fraction was concentrated in 15 c.c. of slightly yellow solution, which, it was to be supposed, would contain all the *d*-tartaric acid present as impurity in the racemic acid. On rendering this slightly alkaline with ammonia, it appeared inactive when examined in a 2-dcm. tube in a polarimeter reading to two minutes of arc.

The most highly purified fraction (300 grams) of this racemic acid was converted into the sodium ammonium salt, and the solution allowed to evaporate spontaneously in twenty open beakers; sixteen dextrorotatory, three lævorotatory, and one optically inactive deposit were thus obtained. Nearly all the dextro-deposits consisted of almost pure *d*-tartrate, whereas the rotatory powers of the lævo-deposits corresponded with an excess of only about 20 per cent. of *l*- over the *d*-tartrate present.

These results seemed to suggest that the separation of the *d*-tartrate might be due to the introduction of some material present in the laboratory dust, and we therefore endeavoured to obtained deposits of large crystals in a dust-free atmosphere. The solution of sodium ammonium *d*- and *l*-tartrates prepared from racemic acid, which had been repeatedly recrystallised as above described, was poured into beakers, which, while still hot, were placed in desiccators so that the condensed vapours would dissolve any crystalline particles present in the atmosphere of the desiccator before the solution was cold ; the solutions were then left to evaporate over sulphuric acid or, in some cases, by aspiration of dry air, filtered through cotton wool, through the desiccator. Under these conditions, the solutions could not be caused to deposit large crystals such as were required for our purpose ; they merely became concentrated to syrups, which, after the lapse of several weeks, became converted into hard, crystalline cakes. The presence of atmospheric dust thus seems necessary to determine the separation of large single crystals of the salt.

In view of the possibility that the atmospheric dust of the ordinary laboratory might contain particles of *d*-tartrates, a further set of crystallisations was carried out in a separate room ; the beakers containing the hot solutions were placed in desiccators, as before, each desiccator containing six or eight beakers, and the next morning, in order to start crystallisation, the covers were removed for a few seconds and then replaced. At the end of the next hour or so, some of the solutions had given deposits of a few (one to four) large crystals ; the beakers containing these solutions were then removed and the crystals examined. The removal of the desiccator covers for this purpose determined the separation of suitable deposits in most of the other solutions. Of the ten deposits thus obtained, five consisted of the dextro-salt, four of the lævo-salt, and one of the inactive material.

Another series of crystallisations was carried out in the same way as the above, using, as before, a solution prepared from carefully purified racemic acid, and at the same time a portion of the same solution was allowed to crystallise in open beakers in the ordinary laboratory ; of nineteen deposits obtained in the desiccators in the separate room, eleven were dextro-, and eight lævo-, rotatory, whilst of nineteen deposits obtained in the beakers freely exposed to the laboratory air, sixteen were dextro-, and only three lævo-, rotatory.

These observations appeared to confirm our suspicion that the preferential crystallisation of the *d*-tartrate was induced by the dust present in the laboratory atmosphere.

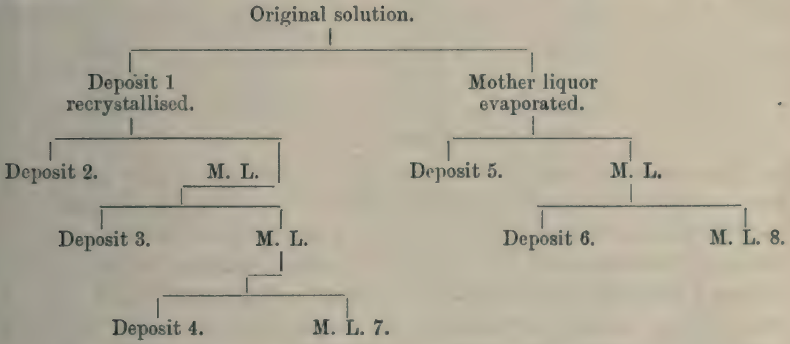
A further investigation of the racemic acid was now carried out with the aid of a polarimeter reading to 0·01° in order to provide information as to the ease with which this acid can be freed from traces of *d*-tartaric acid. The results of this investigation are at present quite inexplicable.

A sample of racemic acid (Kahlbaum's) was divided into five portions, each of 100 grams ; these were separately and systematically fractionally recrystallised from boiling water until the final cold saturated mother liquor from each 100 gram sample occupied rather less than 15 c.c. Each of the five lots of mother liquor was diluted to 15 c.c, and examined in a 2-dcm. tube ; the observed rotatory powers were α_D +0·15°, +0·04°, +0·06°, 0·00°, and 0·00° respectively. This was the first occasion on which we had detected the presence of optically active material in the racemic acid used; the sample was, however, a new one, which might or might not have been identical in character with those previously purchased from the same source. It is very remarkable that whilst three of the 100 gram lots of the same acid gave slightly dextrorotatory mother liquors, the other two yielded mother liquors which were optically inactive.

We were thus led to make a quantitative experiment in order to ascertain whether racemic acid, to which a little *d*-tartaric acid had been added, could be easily separated from the latter by recrystallisation from water. *d*-Tartaric acid (2·24 grams) was dissolved in hot water, together with racemic acid (224 grams) which had been recrystallised several times, and the solution allowed to cool; the crystalline deposit was separated from the still warm solution by the aid of the pump and washed with a little cold water, the combined filtrate and washings being then concentrated to obtain a second deposit. These operations were continued until four successive fractions, each of 40 to 70 grams, were obtained; the mother liquors, which then contained perhaps about 10 grams of acid, were finally evaporated to dryness. The five fractions were then examined polarimetrically, for which purpose 3 grams of each was dissolved in a slight excess of dilute ammonia, the solution diluted to 25 c.c., and examined in a 2-dcm. tube; the observed rotatory powers were respectively $[\alpha]_D$ +0·005°, +0·02°, +0·05°, +0·05°, and +1·42°. In these experiments none of the five fractions was recrystallised, and all were deposited from solutions containing *d*-tartaric acid; the results seemed to indicate that racemic acid which had been crystallised twice (or more) from water could not retain *d*-tartaric acid.

A fresh sample (500 grams) of racemic acid was now crystallised from water, the first deposit washed by the aid of the pump, and recrystallised and washed again; when approximately air-dry, this purified sample (I) weighed 250 grams. After concentrating the combined washings and filtrates from this sample and separating a number of other fractions, we finally obtained a crop of crystals (II) and a mother liquor of about 15 c.c., which together represented all the more soluble matter from the original sample of 500 grams. The last crop of crystals (II) showed no rotatory power when 3 grams were dissolved in dilute ammonia, the solution diluted to 25 c.c., and examined in a 2-dcm. tube; the mother liquor, examined in a 1-dcm. tube, gave α_D +0·14°. Thinking that the sample (I) must be optically inactive, we converted 190 grams of it into the sodium ammonium salt and the solution was allowed to evaporate spontaneously in the laboratory in twenty open beakers; of the deposits thus obtained, eighteen were dextrorotatory and two lævorotatory. It thus seemed proved beyond all reasonable doubt that the deposition of the *d*-salt was caused by particles of laboratory dust; as a final precaution we converted a portion of the sample (I) into its sodium ammonium salt and examined the cold, nearly saturated solution in a 2-dcm. tube. It gave a rotatory power of α_D +0·06°.

In view of this extraordinary result, we resumed our experiments on the crystallisation of racemic acid and determined to examine, not only the mother liquors, but also every fraction of the solid. For this purpose a quantity (400 to 500 grams) of racemic acid was dissolved in hot water and fractionally crystallised as indicated in the following scheme:



Each deposit was washed with cold water and the washings added to the mother liquor, the solution being then concentrated by evaporation. The air-dried deposits were then examined by dissolving 3 grams in dilute ammonia, making up to 25 c.c. with water, and examining in a 2-dcm. tube. The mother liquors were treated with a slight excess of ammonia, diluted to 15 c.c. with water, and examined also in a 2-dcm. tube. The deposits 1, 2, 3, 4, 5, 6 and the mother liquors 7 and 8 gave respectively α_D 0·00°, +0·09°, +0·01°, +0·06°, 0·00°, +0·15°, +0·30°, and +0·09°.

It will be seen from these results that a sample of the acid (1), which contains so small a quantity of a dextrorotatory impurity as to seem optically inactive, may on recrystallisation yield a crop of crystals (2) of relatively high rotatory power. It is also difficult to understand why deposit (3) shows a smaller rotatory power than does deposit (2), and deposit (5) a lower rotatory power than those numbered (2), (3), and (4).

For comparison with these results, those obtained in the following set of fractional crystallisations may be quoted. A sample of racemic acid (183 grams), made up of various portions having rotatory powers of the order of those of fractions (1) to (4) in the previous set, was crystallised from hot water, and the first deposit (I) was separated by filtration; the mother liquor was concentrated, and a second separation (2) similarly obtained. The resulting mother liquor was again concentrated, and made to yield deposits (3) to (6) by a repetition of the processes; the final mother liquor (7) was carefully collected. Each of the fractions into which the sample of acid had been thus divided was polarimetrically examined by dissolving a known weight in 25 c.c. with addition of slight excess of dilute ammonia and examined in a 2-dcm. tube; the results are stated in the following table.

Fraction.	Weight of same in grams.	Weight in 25 c.c. (grams).	α_D.	$[\alpha]_D$.
1	103	2·89	+0·04°	+0·17°
2	23	2·94	+0·06	+0·25
3	21·5	2·09	0·00	0·00
4	21·0	2·14	+0·17	+1·00
5	3	2·48	+0·07	+0·35
6	8	2·42	+0·18	+0·93
7	3·5	by difference	0·00	0·00

The rotatory powers of the successive fractions in this series are seen to follow the same sort of irregular course as in the previous one, so that whilst fractions (1) and (2) are feebly dextrorotatory, (3) is optically inactive and (4) exhibits a comparatively high rotatory power. Several other series of crystallisations were made, all of which led to results very similar to the above and which therefore need not be described in detail.

Although we are not prepared to offer an explanation of the observations recorded in the present paper, we venture to put them forward, having repeatedly confirmed their accuracy, as indicating the difficulties which surround work of the kind and the necessity for the observance of strict caution in drawing conclusions therefrom. It may be provisionally suggested that the preferential deposition of *d*-tartrate from solutions of the sodium ammonium salt prepared from racemic acid, either with or without the addition of dextrose or lævulose, may be due to the presence of a minute excess of *d*-tartaric acid or to the seeding of the solutions by laboratory dust. From the results obtained on fractionally crystallising racemic acid itself, we can only conclude that the elimination of dextrorotatory impurity from the commercial samples of this acid is a matter of great difficulty.

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XV.—*Formation of* cyclo*Hexanone Derivatives from Olefinic Compounds.*

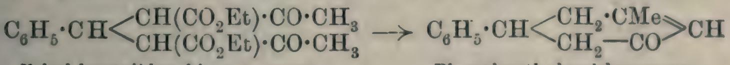
By Siegfried Ruhemann.

In the course of researches on unsaturated compounds, it was found that the sodium derivatives of phenols readily form additive products with the esters of acetylenic acids, ethyl phenylpropiolate, and ethyl acetylenedicarboxylate, and that the substances which are thus produced from the latter ester can be condensed to ethyl benzo-γ-pyronecarboxylate and its homologues. A union of phenols with olefinic monocarboxylic esters or olefinic monoketones cannot be effected. It was thought that such a reaction might take place with olefinic compounds by increasing in them the number of electro-negative groups, as in ethyl benzylideneacetoacetate,

$$C_6H_5\cdot CH{:}C(CO\cdot CH_3)\cdot CO_2Et,$$

and benzylideneacetylacetone, $C_6H_5\cdot CH{:}C(CO\cdot CH_3)_2$.

As stated before (Ruhemann and Watson, Trans., 1904, **85**, 1170), these substances combine with piperidine and other secondary bases to form additive products, which, however, are readily decomposed by water, and yield ethyl benzylidenebisacetoacetate and benzylidenebisacetylacetone. On boiling with dilute potassium hydroxide, these compounds are transformed into 5-phenyl-1-methyl-Δ^1-*cyclo*hexen-3-one (see Knoevenagel, *Annalen*, 1894, **281**, 84), for instance:

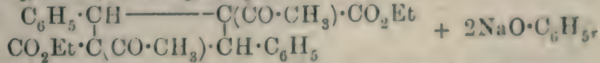


$$C_6H_5\cdot CH{<}\begin{matrix}CH(CO_2Et)\cdot CO\cdot CH_3\\ CH(CO_2Et)\cdot CO\cdot CH_3\end{matrix} \longrightarrow C_6H_5\cdot CH{<}\begin{matrix}CH_2\cdot CMe\\ CH_2-CO\end{matrix}{>}CH$$

Ethyl benzylidenebisacetoacetate. Phenylmethyl*cyclo*hexenone.

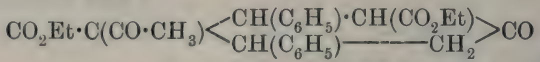
I have, indeed, found that dry sodium phenoxide dissolves in a solution of ethyl benzylideneacetoacetate in absolute ether. The additive product, $C_6H_5\cdot CH(O\cdot C_6H_5)\cdot CNa(\ O\cdot CH_3)\cdot CO_2Et$, which undoubtedly is first formed, does not make its appearance, but a compound is produced which has twice the molecular formula of ethyl benzylideneacetoacetate, namely, $C_{24}H_{28}O_6$. One might be inclined to explain the formation of this substance on the assumption that two molecules of the additive compound condense thus:

$$2C_6H_5\cdot CH(O\cdot C_6H_5)\cdot CNa(CO\cdot CH_3)\cdot CO_2Et =$$



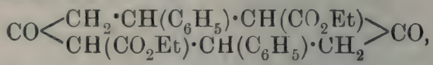
$$\begin{matrix}C_6H_5\cdot CH & \text{———} & C(CO\cdot CH_3)\cdot CO_2Et\\ | & & |\\ CO_2Et\cdot C(CO\cdot CH_3) & \cdot & CH\cdot C_6H_5\end{matrix} + 2NaO\cdot C_6H_5,$$

and yield a derivative of *cyclo*butane. This explanation, however, has to be abandoned for the following reason. If the reaction were to take place in the manner suggested above, one would expect that ethyl benzylidenemalonate, $C_6H_5\cdot CH{:}C(CO_2Et)_2$, would condense with sodium phenoxide in the same way. In this case the phenoxide, indeed, dissolves in an ethereal solution of the ester, but the additive compound is at once decomposed into its components on the addition of water. On the other hand, benzylideneacetylacetone under the influence of sodium phenoxide is transformed into a substance, $C_{24}H_{24}O_4$, which both in its formation and in its behaviour resembles the condensation product of ethyl benzylideneacetoacetate. We are thus led to the conclusion that the acetyl group is concerned in the reaction. This conclusion is supported by the behaviour of ethyl benzoylbenzylideneacetate, $C_6H_5\cdot CH{:}C(CO\cdot C_6H_5)\cdot CO_2Et$. This ester, although undoubtedly forming an additive product, does not lead to a ring formation; the only result is a partial hydrolysis to the corresponding acid. Therefore the compound, $C_{26}H_{28}O_6$, is to be represented thus:

(I.) 

$$CO_2Et\cdot C(CO\cdot CH_3) < \begin{matrix} CH(C_6H_5)\cdot CH(CO_2Et) \\ CH(C_6H_5)\text{------}CH_2 \end{matrix} > CO$$

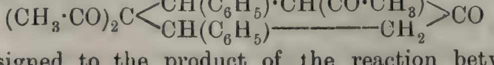
or

(II.) 

$$CO < \begin{matrix} CH_2\cdot CH(C_6H_5)\cdot CH(CO_2Et) \\ CH(CO_2Et)\cdot CH(C_6H_5)\cdot CH_2 \end{matrix} > CO,$$

according as the acetyl groups of one or both molecules of the product of the union betweeen sodium phenoxide and ethyl benzylideneacetoacetate take part in the ring formation. The substance accordingly is either a derivative of *cyclo*hexane or of *cyclo*octane. Either hypothesis would account for the fact that the alcoholic solution of the compound gives a violet coloration with ferric chloride; yet formula I, which characterises the substance as *diethyl acetyldiphenyl*cyclo*hexanonedicarboxylate*, is to be regarded as correct for the following reasons. In the first place, experience has shown that a ring containing six carbon atoms is formed with much greater ease than an eight-membered ring; moreover, it has been found that sodium reacts with the compound to yield a monosodium derivative, whereas for a substance having formula II, the formation of a disodium derivative would be expected. With bromine, the ester, indeed, forms a dibromo-substitution product, $C_{26}H_{26}Br_2O_6$, yet it cannot contain the grouping $\cdot CBr\cdot CO_2Et$, because the alcoholic solution of the bromo-compound gives a violet coloration on the addition of ferric chloride. This circumstance as well as its general resemblance to the original substance, $C_{26}H_{28}O_6$. would suggest that the halogen atoms have entered into one or both benzene nuclei.

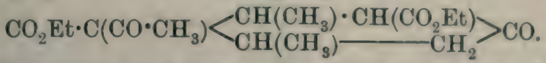
The analogous constitution:



$$(CH_3\cdot CO)_2C < \begin{matrix} CH(C_6H_5)\cdot CH(CO\cdot CH_3) \\ CH(C_6H_5)\text{--------}CH_2 \end{matrix} > CO$$

must be assigned to the product of the reaction between sodium phenoxide and benzylideneacetylacetone; it is therefore *triacetyl*-

*diphenyl*cyclo*hexanone.* Under the same conditions, ethyl ethylideneacetoacetate, $CH_3\cdot CH\colon C(CO\cdot CH_3)\cdot CO_2Et$, yields a condensation product, $C_{16}H_{24}O_6$, which, accordingly, is to be regarded as *diethyl acetyldimethyl*cyclo*hexanonedicarboxylate*,



$$CO_2Et\cdot C(CO\cdot CH_3)<\begin{matrix}CH(CH_3)\cdot CH(CO_2Et)\\ CH(CH_3)\text{———}CH_2\end{matrix}>CO.$$

The yield, however, is rather small, and for this reason I have not studied this substance so closely as the other *cyclo*hexanone derivatives. These substances are also formed on using sodium ethoxide instead of sodium phenoxide, but the reaction in this case is accompanied by great development of heat, and the yield of the cyclic compounds is less satisfactory than with sodium phenoxide. It is most probable that for effecting similar reactions this reagent will be found more convenient than sodium ethoxide.

The *cyclo*hexanone derivative, $C_{26}H_{28}O_6$, is not attacked by potassium hydroxide at the ordinary temperature; on boiling, however, it is readily decomposed, and yields a resinous product from which I have been unable to extract a pure substance. Towards hydrochloric acid the compound is more stable; no change takes place on heating in a closed tube at 100° for several hours, but at 120° it is decomposed into carbon dioxide and a resin. The second *cyclo*hexanone derivative, $C_{27}H_{24}O_4$, on the other hand, is characterised by its great stability towards both potassium hydroxide and hydrochloric acid. All attempts to isolate crystalline substances from the products of the action of phenylhydrazine on those cyclic compounds have failed. This behaviour of the substances is undoubtedly due to the fact that disruption of the ring readily takes place.

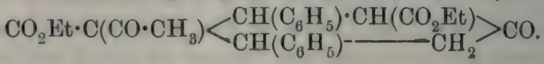
The result arrived at in studying the behaviour of sodium phenoxide or sodium ethoxide towards ethyl benzylideneacetoacetate and benzylideneacetylacetone induced me to ascertain whether, under the influence of these reagents, benzylideneacetone,

$$C_6H_5\cdot CH\colon CH\cdot CO\cdot CH_3,$$

would condense to a cyclic compound. I find, however, that such a reaction does not take place, but the olefinic ketone is decomposed and yields a resinous product. On the other hand, Schiff and Gigli (*Ber.*, 1898, **31**, 1308), in the course of their research on the action of benzylideneaniline on the esters of unsaturated α-hydroxy-acids, showed that an alcoholic solution of sodium ethoxide reacts with a mixture of benzylideneacetone and ethyl oxalate to yield ethyl benzylideneacetoneoxalate, $C_6H_5\cdot CH\colon CH\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$. The same compound, I find, is obtained on using dry sodium ethoxide, suspended in absolute ether, instead of an alcoholic solution of the ethoxide. I was led to repeat the experiment in this way, because it has been ascertained that ethyl oxalate does not take any part in the action of dry sodium ethoxide on a mixture of the ester and benzylideneacetylacetone, and that in this case, also, the *cyclo*hexanone derivative, $C_{27}H_{24}O_4$, is formed.

EXPERIMENTAL.

Diethyl 6-*Acetyl*-1 : 5-*diphenyl*cyclo*hexan*-3-*one*-2 : 6-*dicarboxylate*,



$$CO_2Et\cdot C(CO\cdot CH_3)<\begin{matrix}CH(C_6H_5)\cdot CH(CO_2Et)\\ CH(C_6H_5)-\!\!-\!\!-\!\!-\!\!-CH_2\end{matrix}>CO.$$

This compound is prepared in the following manner: Phenol (19 grams) is mixed with an alcoholic solution of sodium (4·6 grams), and the alcohol is then removed by heating the mixture in a vacuum, first on the water-bath and finally in an oil-bath, at 190—195°. The dry sodium phenoxide which is thus obtained is suspended in absolute ether, and subsequently treated with ethyl benzylideneacetoacetate (43·6 grams). On shaking, the sodium phenoxide gradually dissolves, but before it has completely disappeared, a cloudiness is produced, and, in the course of a day, the whole sets to a semi-solid mass. Water is then added to the product of the reaction, when the solid passes into solution. On evaporation of the ether from the ethereal layer, a yellow oil is left, which soon deposits a mass of crystals. These are collected and washed with a little alcohol, when they become colourless. The substance crystallises from alcohol in prisms, which, after recrystallisation from the same solvent, soften at 122° and melt at 126—127°. The yield of the hexanone derivative amounts to 65 per cent. of the theoretical:

0·2075 gave 0·5445 CO_2 and 0·1225 H_2O. C = 71·57; H = 6·55.

$C_{26}H_{28}O_6$ requires C = 71·56; = 6·42 per cent.

Molecular-weight determinations were carried out by the cryoscopic method with the following results:

0·3734 in 31·005 benzene gave $\Delta t = -0·135°$. M.W. = 437.

0·4135 ,, 31·476 acetic acid gave $\Delta t = -0·116°$. M.W. = 439.

$C_{26}H_{28}O_6$ requires M.W. = 436.

The compound is readily soluble in ether, carbon disulphide, benzene, chloroform, or hot alcohol, and moderately so in cold alcohol; the alcoholic solution gives a reddish-violet coloration on the addition of ferric chloride. It dissolves in cold concentrated sulphuric acid, yielding a yellow solution, which, on warming, turns a deep red. The *cyclo*hexanone derivative is not attacked by hydrochloric acid on being heated with the concentrated acid at 100° in a closed tube for several hours; at 120°, however, decomposition takes place, and there is formed, besides carbon dioxide, a tarry product. This, after some time, sets to a brown, brittle solid; all attempts to isolate from it a pure substance failed. The study of the action of potassium hydroxide likewise furnished unsatisfactory results. At the ordinary temperature, no change is produced by the alkali, even on being in contact with it for many hours; on boiling with the alkali for a few minutes, however, the odour of benzaldehyde is developed, and a dark oil is formed which solidifies when cold. On adding dilute hydrochloric acid to the alkaline filtrate, carbon dioxide is evolved, and a yellow resin is precipitated. I have repeatedly carried out this reaction, varying the amount and dilution of the potassium hydroxide, but in each case resinous products were formed.

Phenylhydrazine readily reacts with the cyclic compound at the temperature of the water-bath, yielding an oil; on adding acetic acid, an amorphous solid is precipitated, from which I have been unable to extract any crystalline substance.

Sodium acts on the cyclic substance with evolution of hydrogen and formation of the *sodium* derivative, $C_{26}H_{27}O_6Na$. The metal, in the form of wire, dissolves very slowly in a solution of the compound in absolute ether, and colourless needles gradually separate; the reaction is almost complete in two days. The suspension of the sodium derivative in ether is then poured off from the unattacked metal, the crystals collected, washed with dry ether, and dried in a vacuum over sulphuric acid. The sodium derivative is prepared more readily by shaking a solution of the compound, $C_{26}H_{28}O_6$, in absolute ether with an excess of dry sodium ethoxide, and, after a few minutes, collecting from the undissolved ethoxide. The filtrate gradually separates colourless needles, which, in the course of a day, increase in quantity. On analysis, both specimens gave the same result. The first refers to the specimen obtained by the action of the metal, the second to the product prepared by means of sodium ethoxide:

0·0875 gave 0·0140 Na_2SO_4. Na = 5·18.
0·2085 ,, 0·0345 Na_2SO_4. Na = 5·36.
$C_{26}H_{27}O_6Na$ requires Na = 5·02 per cent.

The sodium derivative is decomposed by water, even when cold, with formation of the original compound, $C_{26}H_{28}O_6$.

Action of Bromine on Diethyl 6-*Acetyl*-1 : 5-*diphenyl*cyclo*hexan*-3-*one*-2 : 6-*dicarboxylate.*

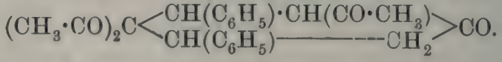
On adding bromine (0·8 gram) to a solution of the *cyclo*hexanone compound (2 grams) dissolved in carbon disulphide, hydrogen bromide is evolved, and, after a few hours, the halogen disappears. On concentration of the solution in a vacuum desiccator, a solid separates, which dissolves in hot alcohol and, on cooling, crystallises in colourless prisms melting at 154—155°:

0·2085 gave 0·3997 CO_2 and 0·0830 H_2O. $C = 52·28$; $H = 4·42$.
0·3505 „ 0·2205 AgBr. $Br = 26·77$.
$C_{26}H_{26}O_6Br_2$ requires $C = 52·52$; $H = 4·38$; $Br = 26·94$ per cent.

The yield of this compound is almost theoretical, but it is greatly reduced if an excess of bromine is used, when at the same time another substance is formed. This is very soluble in carbon disulphide, and, on complete removal of the latter, is left behind as a viscous product, which slowly solidifies.

The *dibromo*-derivative, $C_{26}H_{26}O_6Br_2$, is sparingly soluble in ether, but readily so in hot alcohol. The alcoholic solution gives a violet coloration on the addition of ferric chloride; in this respect, and also in its behaviour towards potassium hydroxide, it resembles the original substance. These facts, as pointed out in the introduction, lead to the view that the halogen has entered into either one or both benzene nuclei of the *cyclo*hexanone compound.

2 6 : 6-*Triacetyl*-1 : 5-*diphenyl*cyclo*hexan*-3-*one*,



$$(CH_3\cdot CO)_2C<\begin{matrix}CH(C_6H_5)\cdot CH(CO\cdot CH_3)\\ CH(C_6H_5)\text{———————}CH_2\end{matrix}>CO.$$

This substance is formed from benzylideneacetylacetone by means of sodium ethoxide or sodium phenoxide, but, as stated before (p. 111), the latter is preferable. The dry sodium phenoxide (from 1·2 grams of sodium and 5 grams of phenol), prepared in the same way as in the previous case, is suspended in absolute ether and mixed with the olefinic diketone (9·8 grams). After a short time, the phenoxide will have completely disappeared, and an orange solution is formed, from which no solid separates. The mixture is kept overnight, the ether is then distilled from the water-bath, and water added to the residue, when a crystalline product remains undissolved. This is soluble in a large quantity of boiling alcohol, and, on cooling, gradually separates in colourless prisms, which melt not quite sharply at 188—189°:

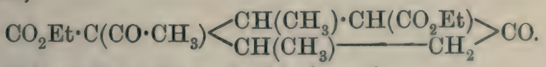
0·2030 gave 0·5685 CO_2 and 0·1196 H_2O. $C = 76·38$; $H = 6·54$.
0·2008 „ 0·5634 CO_2 „ 0·1200 H_2O. $C = 76·52$; $H = 6·64$.
$C_{24}H_{24}O_4$ requires $C = 76·60$; $H = 6·38$ per cent.

The substance is sparingly soluble in boiling alcohol, moderately so in hot benzene or glacial acetic acid, but readily so in chloroform. The alcoholic solution of this compound, like the one of the former *cyclo*hexanone derivative, gives a reddish-violet coloration on the addition of ferric chloride. *Triacetyldiphenyl*cyclo*hexanone* is very stable towards both hydrochloric acid and potassium hydroxide, and in this respect differs markedly from the former compound, $C_{26}H_{28}O_6$. Only slight decomposition takes place on heating it with the acid at 150—160°. Potassium hydroxide dissolves it on warming, and yields a yellow solution, from which it is precipitated unchanged by hydrochloric acid. Decomposition, however, takes place if the substance is boiled with the alkali for some time, when the odour of benzaldehyde is perceptible; this points to a disruption of the hexanone ring.

On digesting the compound with phenylhydrazine on the water-bath, it dissolves, yielding a red oil; if this is mixed with acetic acid a dark precipitate is formed, which is readily soluble in alcohol or ether, but separates from the concentrated solutions in the form of a resin.

Action of Sodium Phenoxide on Ethyl Ethylideneacetoacetate.

This reaction was effected in the same way as in the previous cases. To dry sodium phenoxide (prepared from 4·6 grams of sodium and 18·8 grams of phenol), suspended in absolute ether, ethyl ethylideneacetoacetate (31·2 grams) is slowly added. Heat is developed, and the phenoxide gradually dissolves, forming a yellow solution, which, after being kept for a day, is poured into water. On evaporation of the ether from the ethereal solution, an oil is left behind, which, when distilled in a vacuum, begins to boil at 78°; the thermometer, then, rises continually, and between 145° and 235° a yellow oil passes over from which I have been unable to isolate a substance distilling at a constant temperature. The aqueous layer from the product of the reaction, when treated with an excess of dilute hydrochloric acid, yields an oil, which is fractionated under diminished pressure. A pure substance is thus obtained which boils at 258—260°/28 mm. It is a viscous oil, which, after some time, sets to a semi-solid. According to the mode of formation, the compound is most probably to be regarded as *diethyl* 6-*acetyl*-1:5-*dimethyl*cyclo*hexan*-3-*one*-2:6-*dicarboxylate*,



$$CO_2Et\cdot C(CO\cdot CH_3)<\begin{matrix}CH(CH_3)\cdot CH(CO_2Et)\\ CH(CH_3)\text{———————}CH_2\end{matrix}>CO.$$

The analytical results agree with this formula:

0·2040 gave 0·4610 CO_2 and 0·1435 H_2O. $C = 61·63$; $H = 7·81$.

$C_{16}H_{24}O_6$ requires $C = 61·54$; $H = 7·69$ per cent.

The above constitution, moreover, is supported by the fact that the alcoholic solution of the substance gives a red coloration on the addition of ferric chloride. The yield is small, only 25—30 grams being formed from 63 grams of ethyl ethylideneacetoacetate.

Action of Sodium Phenoxide on Ethyl Benzylidenemalonate.

On adding ethyl benzylidenemalonate to dry sodium phenoxide, suspended in absolute ether, a clear solution is produced after a short time, which points to the formation of an additive compound. This however, is unstable, and, on shaking the ethereal solution with water, it dissociates into its components, ethyl benzylidenemalonate and sodium phenoxide. The former substance is left behind on evaporation of the ether from the ethereal layer; the phenol can be isolated from the aqueous solution. In this way were recovered almost the same weights of the compounds as had been used for the experiment. This result indicates that no other product is formed in the reaction.

Action of Sodium Phenoxide on Ethyl Benzoylbenzylideneacetate.

As stated before (p. 110), this reaction does not yield a cyclic compound, but the sodium phenoxide forms with the ester an additive product, because it dissolves in a solution of ethyl benzoylbenzylideneacetate in absolute ether. In the course of a day, a solid separates which is the sodium salt of benzoylbenzylideneacetic acid,

$$C_6H_5\cdot CH{:}C(CO\cdot CH_3)\cdot CO_2H.$$

The acid is precipitated from the aqueous solution of the salt by the addition of dilute hydrochloric acid. It is readily soluble in alcohol or ether, and crystallises from dilute alcohol in colourless needles, which melt and evolve carbon dioxide at 154—155°:

0·2108 gave 0·5870 CO_2 and 0·0950 H_2O. C = 75·94; H = 5·00.

$C_{16}H_{12}O_3$ requires C = 76·19; H = 4·76 per cent.

Ethyl Benzylideneacetoneoxalate, $C_6H_5\cdot CH{:}CH\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et$.

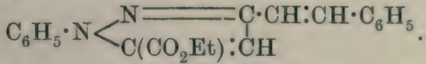
Benzylideneacetone does not unite with sodium phenoxide; it dissolves, indeed, in a solution of the ketone in absolute ether, but the solution immediately turns dark and yields a black, resinous product.

Whereas benzylideneacetylacetone reacts with ethyl oxalate, in the presence of sodium ethoxide, to form the same compound $C_{24}H_{24}O_4$, as is produced without the use of ethyl oxalate, benzylideneacetone yields ethyl benzylideneacetoneoxalate on treatment with these reagents. This reaction has been already studied by Schiff and Gigli (*Ber.*, 1198, **31**, 1308), who effected it in alcoholic solution. I have repeated this experiment, using dry sodium ethoxide and a solution of the ketone in absolute ether. The result, however, does not differ from that obtained by these chemists. The solution which is formed on adding ethyl oxalate (15 grams) to dry sodium ethoxide (prepared from 2·3 grams of sodium), suspended in absolute ether, turns yellow when it is mixed with benzylideneacetone (14·6 grams), dissolved in absolute ether, and deposits a yellow solid. This is the sodium derivative of ethyl benzylideneacetoneoxalate. Dilute hydrochloric acid transforms it into the free ester. The yield is 80—85 per cent. of the theoretical. The ester is sparingly soluble in cold, but readily so in hot, alcohol, and crystallises in yellow prisms. The melting point (84°) as well as its properties and the following analysis agree with Schiff and Gigli's observations:

0·2017 gave 0·5047 CO_2 and 0·1052 H_2O. C = 68·24; H = 5·79.

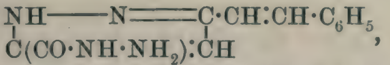
$C_{14}H_{14}O_4$ requires C = 68·29; H = 5·69 per cent.

These chemists also examined the action of phenylhydrazine on the ester, and obtained the pyrazole derivative:



$$C_6H_5{\cdot}N<\begin{matrix}N{=\!=\!=}C{\cdot}CH{:}CH{\cdot}C_6H_5\\ C(CO_2Et){:}CH\end{matrix}.$$

On using hydrazine itself, the *hydrazide* of *styrylpyrazolecarboxylic acid*,



$$\begin{matrix}NH{-\!-}N{=\!=\!=}C{\cdot}CH{:}CH{\cdot}C_6H_5\\ C(CO{\cdot}NH{\cdot}NH_2){:}CH\end{matrix},$$

is formed. This is prepared by slowly adding hydrazine hydrate to ethyl benzylideneacetoneoxalate, dissolved in alcohol; the yellow solution first turns red, then light yellow, and deposits a solid which crystallises from alcohol in almost colourless plates, melting at 225—226°:

0·1938 gave 0·4478 CO_2 and 0·0919 H_2O. C = 63·01; H = 5·26.
0·2110 ,, 45·4 c.c. N_2 at 18° and 758 mm. N = 24·76.

$C_{12}H_{12}ON_4$ requires C = 63·14; H = 5·26; N = 24·56 per cent.

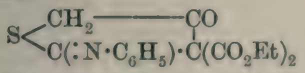
The substance is insoluble in water or ether, but dissolves, although sparingly, in boiling alcohol.

University Chemical Laboratory,
Cambridge.

XVI.—*The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids. Part II.*

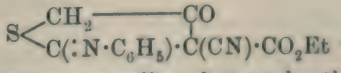
By Siegfried Ruhemann.

I have recently shown (Trans., 1908, **93**, 621) that the thioanilides of diethyl methanetricarboxylate and ethyl cyanomalonate react with ethyl chloroacetate to yield cyclic compounds, which were represented thus:



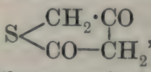
$$S<\begin{matrix}CH_2{-\!-\!-}CO\\ C({:}N{\cdot}C_6H_5){\cdot}C(CO_2Et)_2\end{matrix}$$

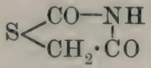
and



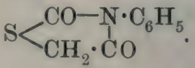
$$S<\begin{matrix}CH_2{-\!-\!-}CO\\ C({:}N{\cdot}C_6H_5){\cdot}C(CN){\cdot}CO_2Et\end{matrix}.$$

It was stated, also, that these substances are yellow, but, under the influence of potassium hydroxide, become colourless. This behaviour was explained by the assumption of the existence of the compounds in two isomeric forms. With the object of ascertaining whether this view is correct, I have subjected those substances to a closer study, which is recorded in this paper.

The above-mentioned compounds may be regarded as derivatives of the type , which indicates the similarity of their structure to 2 : 4-diketotetrahydrothiazole (I) and its phenyl derivative (II):



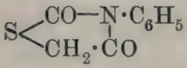
(I.)



(II.)

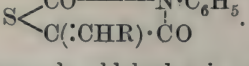
2 : 4-Diketotetrahydrothiazole was discovered by Heintz (*Annalen*, 1865, **136**, 223), who prepared it by boiling ethyl thiocyanoacetate with hydrochloric acid. The same chemist stated that this ester, on distillation, partly decomposes. I have observed, however, that under diminished pressure it boils unchanged. 2 : 4-Diketo-3-phenyltetrahydrothiazole is formed, according to Liebermann and Völtzkow (*Annalen*, 1881, **207**, 137), by heating chloroacetic acid with either phenylthiourethane or phenylthiocarbimide.

With the view of examining whether one of the ketonic groups of 2 : 4-diketo-3-phenyltetrahydrothiazole is reactive, I have treated the compound with ethyl malonate as well as with ethyl acetoacetate, using piperidine as a catalyst, but no condensation takes place; the base decomposes the substance without the esters being attacked, piperidylformanilide and thioglycollic acid being formed:

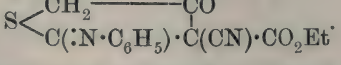


$$+ C_5H_{11}N + H_2O = C_5H_{10}N\cdot CO\cdot NH\cdot C_6H_5 + SH\cdot CH_2\cdot CO_2H.$$

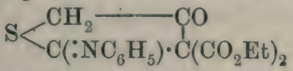
With aldehydes, 2 : 4-diketo-3-phenyltetrahydrothiazole forms the condensation products:



The same behaviour towards aldehydes is exhibited by the yellow substance



The fact that the colourless product formed from it with aldehydes under the influence of alkalis yields the same substances leads to the conclusion that the two compounds which had been regarded as different are in fact identical. A closer examination has confirmed this view. In the preparation of the substance from ethyl chloroacetate and the thioanilide of ethyl cyanoacetate, animal charcoal was used to decolorise the dark alcoholic solutions, and the yellow crystals which separated on cooling retained their colour even after frequent recrystallisations. I now find that the substance may be obtained colourless, if it is crystallised several times from alcohol without the use of animal charcoal, and that this product is, in every respect, identical with the colourless crystals obtained before from the yellow specimen. This result points to the view that also the substance



exists in one form only, although, as yet, I have been unable to remove the yellow colour by crystallisation of the condensation product. This, like the former compound, condenses with aldehydes, and, with bromine, forms a dibromo-substitution product.

EXPERIMENTAL.

Ethyl Thiocyanoacetate, $CNS{\cdot}CH_2{\cdot}CO_2Et$.

Heintz (*loc. cit.*), who obtained this ester by the action of potassium thiocyanate on ethyl monochloroacetate, stated that, on distillation at the ordinary temperature, it suffered partial decomposition, the distillate turning red on exposure to the air; under diminished pressure he gave the boiling point as about 180°, and noticed that a considerable residue remained behind in the retort, as was the case on distillation at the ordinary pressure. I find, however, that under 10 mm. pressure the ester distils unchanged at 117° as a colourless oil, and that the yield is almost theoretical:

0·2025 gave 0·3060 CO_2 and 0·0884 H_2O. C = 41·21; H = 4·85.
0·3050 ,, 26 c.c. N_2 (moist) at 20° and 762 mm. N = 9·77.
$C_5H_7O_2NS$ requires C = 41·38; H = 4·82; N = 9·66 per cent.

On boiling the ester with concentrated hydrochloric acid, it is transformed into 2 : 4-diketotetrahydrothiazole.

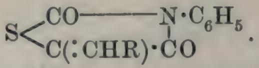
2 : 4-*Diketo-3-phenyltetrahydrothiazole.*

This substance is readily formed from chloroacetic acid and phenylurethane according to Liebermann and Völtzkow's directions (*loc. cit.*). As stated before (p. 118), it does not condense with ethyl malonate or ethyl acetoacetate in the presence of piperidine; the esters are not attacked, and the piperidine decomposes the cyclic compound into *piperidylformanilide* and thioglycollic acid. The former separates from the alcoholic solution of the mixture on being kept for a day, and crystallises from alcohol in long, colourless needles melting at 170—171°:

0·2012 gave 0·5206 CO_2 and 0·1445 H_2O. C = 70·56; H = 7·98.
0·2260 ,, 28·5 c.c. N_2 (moist) at 21° and 740 mm. N = 13·95.
$C_{12}H_{16}ON_2$ requires C = 70·59; H = 7·84; N = 13·72 per cent.

The mother liquor from the anilide contains thioglycollic acid. In order to isolate it, the filtrate is acidified and extracted with ether, the ethereal layer is then agitated with potassium hydroxide, and the alkaline solution treated with an excess of dilute sulphuric acid. The ethereal extract of this solution, on evaporation of the ether, yields an oil, the aqueous solution of which gives with ferric chloride and ammonia the reddish-violet coloration characteristic of thioglycollic acid.

2 : 4-Diketo-3-phenyltetrahydrothiazole condenses with aldehydes on adding a few drops of piperidine to the alcoholic solution of the mixture of the reagents, and the compounds which are formed have the general formula :



$$S<\begin{matrix}CO\text{———}N\cdot C_6H_5\\ C(:CHR)\cdot CO\end{matrix}.$$

Thus, on using benzaldehyde, the *benzylidene* derivative is produced, which is almost insoluble in cold alcohol, but dissolves, although sparingly, in boiling alcohol, and, on cooling, separates in colourless, curved needles which melt at 208—209° :

0·1961 gave 0·4910 CO_2 and 0·0693 H_2O. C = 68·28 ; H = 3·92.
0·2287 ,, 9·6 c.c. N_2 (moist) at 18° and 775 mm. N = 5·07.
$C_{16}H_{11}O_2NS$ requires C = 68·33 ; H = 3·91 ; N = 4·98 per cent.

With salicylaldehyde, the *salicylidene* derivative is formed, which crystallises from boiling alcohol in deep yellow needles melting not quite sharply at 238—239° :

0·2056 gave 0·4858 CO_2 and 0·0725 H_2O. C = 64·44 ; H = 3·95.
0·2300 ,, 9·6 c.c. N_2 (moist) at 16° and 754 mm. N = 4·82.
$C_{16}H_{11}O_3NS$ requires C = 64·64 ; H = 3·70 ; N = 4·71 per cent.

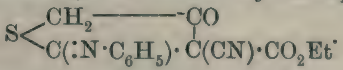
The condensation product of 2 : 4-diketo-3-phenyltetrahydrothiazole with piperonal is sparingly soluble in boiling alcohol, from which, on cooling, it crystallises in yellow needles melting at 207—208° :

0·2312 gave 8·8 c.c. N_2 (moist) at 18° and 753 mm. N = 4·35.
$C_{17}H_{11}O_4NS$ requires N = 4·31 per cent.

The *cinnamylidene* derivative is almost insoluble in cold alcohol, but dissolves in a large quantity of boiling alcohol, and, on cooling, separates in long, yellow needles melting at 214° :

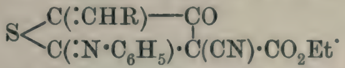
0·2024 gave 0·5225 CO_2 and 0·0765 H_2O. C = 70·40 ; H = 4·20.
0·2527 ,, 10 c.c. N_2 (moist) at 18° and 760 mm. N = 4·57.
$C_{18}H_{13}O_2NS$ requires C = 70·36 ; H = 4·23 ; N = 4·56 per cent.

Ethyl 2-Phenylimino-3-cyano-4-ketotetrahydrothiophen-3-carboxylate,



$$\mathrm{S}\Big\langle\begin{array}{l}\mathrm{CH_2}\text{———}\mathrm{CO}\\ \mathrm{C(:N\cdot C_6H_5)\cdot C(CN)\cdot CO_2Et}\end{array}.$$

Like 2:4-diketo-3-phenyltetrahydrothiazole, this substance condenses with aldehydes to yield compounds with the general formula:



$$\mathrm{S}\Big\langle\begin{array}{l}\mathrm{C(:CHR)}\text{—}\mathrm{CO}\\ \mathrm{C(:N\cdot C_6H_5)\cdot C(CN)\cdot CO_2Et}\end{array}.$$

The *benzylidene* derivative is formed on adding a few drops of piperidine to the hot alcoholic solution of the mixture of the cyclic compound and benzaldehyde. The solution turns red and deposits, while still hot, a yellow solid, which is very sparingly soluble in boiling alcohol, moderately so in glacial acetic acid, and crystallises from either solution, on cooling, in hair-like, curved needles melting at 284°:

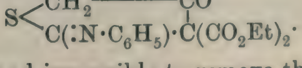
0·2055 gave 0·5045 CO_2 and 0·0810 H_2O. C = 65·95; H = 4·38.
0·2425 „ 16·4 c.c. N_2 (moist) at 15° and 740 mm. N = 7·70.
$C_{21}H_{16}O_3N_2S$ requires C = 67·02; H = 4·26; N = 7·45 per cent.

The *salicylidene* derivative, prepared in a similar way, is sparingly soluble in boiling alcohol, moderately so in boiling glacial acetic acid, and, on cooling, crystallises in aggregates of yellow needles, which begin to decompose at about 240° and melt at 252° to a brown liquid:

0·2052 gave 0·4825 CO_2 and 0·0766 H_2O. C = 64·12; H = 4·14.
0·2305 „ 14·6 c.c. N_2 (moist) at 20° and 745 mm. N = 7·10.
$C_{21}H_{16}O_4N_2S$ requires C = 64·28; H = 4·08; N = 7·14 per cent.

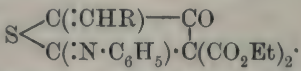
It has been mentioned before (p. 118) that the colourless substance which is formed from the yellow condensation product of ethyl chloroacetate with the thioanilide of ethyl cyanomalonate, on treatment with alkalis, reacts with aldehydes to yield the same compounds, and that this fact points to the view that the colourless and the yellow products are identical. It was found impossible to remove the yellow colour by repeatedly boiling the alcoholic solutions of the compound with animal charcoal, but this was finally effected by recrystallising the condensation product four times from alcohol without the use of animal charcoal. The crystals which were obtained showed all the properties of the colourless specimen. It follows, therefore, that the yellow colour of the compound is due to an impurity.

Diethyl 2-Phenylimino-4-ketotetrahydrothiophen-3-dicarboxylate,



$$\mathrm{S}\Big\langle\begin{array}{l}\mathrm{CH_2}\text{———}\mathrm{CO}\\ \mathrm{C(:N\cdot C_6H_5)\cdot C(CO_2Et)_2}\end{array}.$$

Although it was found impossible to remove the yellow colour from the condensation product of ethyl chloroacetate with the thioanilide of diethyl methanetricarboxylate by recrystallisation from alcohol with or without the use of animal charcoal, yet, after the experience made with the former substance, there cannot be any doubt that it is identical with the one which is formed from it on treatment with potassium hydroxide. This cyclic compound, like the other, condenses with aldehydes in the presence of piperidine, forming the substances having the general formula:



$$S\left<\begin{array}{l} C(:CHR)\text{—}CO \\ C(:N\cdot C_6H_5)\cdot C(CO_2Et)_2\cdot \end{array}\right.$$

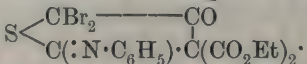
The *benzylidene* derivative separates on keeping the alcoholic solution of the mixture of the reagents overnight. It is moderately soluble in boiling alcohol, and, on cooling, crystallises in faintly yellow needles which melt at 164°:

0·2057 gave 0·4910 CO_2 and 0·0922 H_2O. C = 65·10; H = 4·98.
0·2385 „ 7·4 c.c. N_2 (moist) at 24° and 743 mm. N = 3·39.
$C_{23}H_{21}O_5NS$ requires C = 65·24; H = 4·96; N = 3·31 per cent.

The *salicylidene* derivative is fairly readily soluble in hot alcohol, sparingly so in benzene, and crystallises from this solution in yellow needles which melt at 204°:

0·2742 gave 7·8 c.c. N_2 (moist) at 20° and 757 mm. N = 3·24.
$C_{23}H_{21}O_6NS$ requires N = 3·19 per cent.

Bromine reacts with the compound $C_{16}H_{17}O_5NS$ to form *diethyl 5-dibromo-2-phenylimino-4-ketotetrahydrothiophen-3-dicarboxylate*,



$$S\left<\begin{array}{l} CBr_2\text{———}CO \\ C(:N\cdot C_6H_5)\cdot C(CO_2Et)_2\cdot \end{array}\right.$$

This is prepared by adding the halogen (2 mols.) to the solution of the cyclic compound (1 mol.) in chloroform; hydrogen bromide is evolved, and, on removal of the solvent in a vacuum, a yellow solid is left behind, which crystallises from light petroleum in clusters of light yellow needles. These, after being twice recrystallised from the same solvent, melt at 140°:

0·2138 gave 0·3066 CO_2 and 0·0595 H_2O. C = 39·11; H = 3·09.
0·2855 „ 7·8 c.c. N_2 (moist) at 16° and 745 mm. N = 3·12.
0·2698 „ 0·2035 AgBr. Br = 32·10.
$C_{16}H_{15}O_5NBr_2S$ requires C = 38·95; H = 3·04; N = 2·84; Br = 32·45 per cent.

The bromo-derivative is very soluble in chloroform or benzene, and sparingly so in cold, but readily so in hot, light petroleum.

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CAMBRIDGE.

XVII.—*The Hydration of Precipitates.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

NOTHING is known at present as to the state of hydration of substances at the moment of their precipitation, although the natural impression is that those substances which form bulky precipitates must be in a highly hydrated condition. If this were proved to be the case, a high degree of hydration in the case of substances whilst actually in solution would be rendered more probable. The work on emulsions, of which an account was laid before the Society (Trans., 1907, **91**, 2001), seemed to offer the means of obtaining information on this point.

Finely-divided solids, such as recently-formed precipitates, were found to emulsify oils, and by suitably adjusting the proportions of precipitate and oil, an emulsion can be obtained which is of the same average density as the liquid. By determining this density, (S), and ascertaining the volume and weight of the oil, (V' and W'), as well as the volume and weight of the precipitate after drying, (V and W), we can deduce the volume and weight of the water, (v and w), which is combined with it when in the freshly precipitated condition, for

$$W + w + W' = S(V + v + V')$$

and substituting sw for v (s being the specific gravity of the combined water), we get

$$w(1 - Ss) = S(V + V') - (W + W').$$

The equation cannot be solved by any one set of determinations without assuming a value for the specific gravity of the combined water, but such an assumption may be obviated by getting two sets of determinations in two liquids of different specific gravities.

After examining a number of precipitates, the only one that appeared to offer any chance of success was the basic sulphate of copper precipitated by lime-water. This emulsifies paraffin oil very easily, and it may be precipitated in liquids the specific gravity of which is varied by the presence of various quantities of sodium sulphate. Several series of experiments, however, failed to give any satisfactory results, owing, it was found, to the fact that the basic sulphate combined with the sodium and calcium sulphates present to form a complicated double salt, and it was not until after the nature and conditions of formation of this double salt had been investigated that success was obtained.

An account of this preliminary investigation has already appeared (Trans., 1907, **91**, 1988), from which it will be seen that the substance obtained when lime-water is added to copper sulphate until alkalinity is just attained is, approximately, $10CuO,SO_3,1{\cdot}35CaSO_4$, but that, if sodium sulphate is present, the precipitate consists of

$$10CuO,SO_3,CaSO_4,Na_2SO_4,$$

the composition remaining unaffected by the proportion of sodium sulphate present, when this varies between the limits of 15 and $45Na_2SO_4$ for every $10CuSO_4$ taken. (The limits may be more extended, but the determinations were not pushed further.) The sodium and calcium sulphate may, perhaps, be interchangeable, being $2[(Ca,Na_2)SO_4]$, for the relative proportions of them found in the different experiments varied a good deal; they are certainly combined in a loose way with the rest of the molecule, and are gradually removed by washing with water.

This latter fact accounts for a deficit in the proportion of neutral sulphate contained in the sample of the compound prepared for the determination of its density in the present work, for solutions from which it was precipitated had to be very dilute, so as to obviate the possibility of any of the calcium sulphate formed in the reaction being deposited (*loc. cit.*, p. 1993). Copper sulphate solution was mixed with sodium sulphate in the proportion of $10CuSO_4 : 30Na_2SO_4$, and lime-water, diluted to half-saturation strength, added to alkalinity. The precipitate was filtered by means of a Berkefeld filter, access of air being avoided as far as possible; and then, without washing, it was dried by exposure to sodium hydroxide. When dry, it was powdered, washed once, and dried again. The composition according to analysis was $10CuO,SO_3$, $0{\cdot}776CaSO_4$, $0{\cdot}864Na_2SO_4$, $11{\cdot}746H_2O$.

Its specific gravity at 15° was 2·699664. This was taken in "solar distillate," which had been purified by digestion with nitric acid, sodium hydroxide and sodium, successively: its specific gravity was 0·857589.

Three series of determinations were made on the emulsification of this oil by the freshly precipitated substance, the proportions of sodium sulphate present being 15, 30 and $45Na_2SO_4$, respectively, to every $10CuSO_4$. The copper was precipitated with half-strength lime-water, and the volume was adjusted so that a unit volume contained in each case the same weight of precipitate. Eight of nine lots of 400 c.c. of each of these preparations were put into graduated stoppered jars, and different volumes of "solar distillate" added to them. Each was then emulsified by churning it with a syringe with a rose jet, and then left in the jar for the emulsion to rise or fall, as the case might be. As the precipitate is attacked by carbon dioxide, the churning had to be restricted as far as possible, only three strokes of the syringe being given. After syringing, bubbles of air are present in the liquid, which carry some of the emulsion to the top; these can be eliminated with a little manipulation, and then the emulsion rises or sinks as a whole, showing a clear-cut surface against the rest of the liquid. The approximate amount of oil required had to be determined by preliminary experiments, and in the final ones these amounts were so adjusted that in each series half the emulsions were heavier than the liquid, and half lighter. After being left to stand for from eight to twenty-four hours, readings were taken of the extent to which the emulsions had sunk or risen, and these readings, when plotted against the volume of oil present, gave the equilibrium point, or that of the volume of oil requisite to ensure neither sinking nor rising. The liquids were then gently agitated, left to settle, and another set of readings taken. The mean of three or four such series of observations was finally adopted, and then the liquids were filtered from the emulsions, and their specific gravities determined.

The emulsions must not be left too long before taking the readings, for the emulsions which are heavier or lighter than the liquid will eventually sink or rise, so as to occupy nearly the same volumes, and the diagram representing their position will then consist of two discontinuous lines, and will be useless for determining the equilibrium point. It should also be mentioned that satisfactory results can only be obtained by manipulating all the liquids in exactly the same way, and doing all the series of experiments at the same time.

In the 400 c.c. of liquid in each series, the weight of dry precipitate (W) of the composition given above by the analysis, and as determined by the weight of copper sulphate taken, was 0·81789 gram, and its volume, V, was, consequently, 0·30297 c.c. The other values in the three series, A, B and C, were as follows:

	"Solar distillate."		Sp. gr. of liquid.
	V'.	W'.	S.
A	3·704 c.c.	3·1765 grams	1·004570
B	3·614 ,,	3·1002 ,,	1·007550
C	3·516 ,,	3·0153 ,,	1·011288

From these the weight, w, of the water originally combined with the 0·81789 gram of the dry precipitate is found to be:

From *A* and *B*	0 467
,, *B* ,, *C*	0·208
,, *A* ,, *C*	0·329
Mean	0·335

This represents 40·96 parts of water to 100 of dry precipitate, which, with the water still present in this so-called dry precipitate, gives a percentage of 40·4 as the total water in the freshly precipitated substance. Its composition, therefore, using whole numbers, would be

$$10CuO,SO_3,CaSO_4,Na_2SO_4,42H_2O.$$

The value for the degree of hydration of this substance can have no pretension to exactness, and cannot be accepted as more than giving an indication of the order of magnitude of the equivalents of water present. The individual values for the different pairs of observations lead to numbers ranging for 33 to 59 H_2O; such a range, however, is well within the limits of experimental error, for it corresponds with a total error of only 0·005 c.c. in the volumes of the oil, and greater errors might have been expected, even although these volumes were deduced by the diagrammatic treatment of several series of observations. The necessary dilution of the liquids, and the smallness of the range of available alterations in the density of the liquid, rendered it impossible to obtain more accurate results.

As to the degree of hydration: 42 equivalents of water in a molecule is certainly a large number, but the molecule itself is a highly complex one, and the 40 per cent. of its weight which this water represents is not a very large percentage, being exceeded in the case of many of the simpler crystalline salts: so that the facts elucidated do not afford much food for comment.

From the weight of water in the precipitate, the specific gravity of that water can be calculated, and, using the mean value for the former, ($w = 0·335$), the three series of experiments lead to 0·9037, 0·9049 and 0·9035, mean 0·904, as the sp. gr. of the combined water, or, rather, of the $30H_2O$ beyond the $12H_2O$ in the dried precipitate. Considering the circumstances of the case, these values are remarkably concordant, and are also remarkably close to that of ice, which for 15°/15° is probably 0·916. There can be no doubt, therefore, that the water in the precipitate is in the solid condition, as it is known to be in the majority of highly hydrated crystals; indeed, the values as they stand indicate that the water in combining has expanded even rather more than water does when it freezes.

The amount of water in these bulky precipitates affords no sufficient explanation of their bulkiness; this must be due to some cause, such as the shape and character of the particles. The above data, for instance, lead to 1·71 as the sp. gr. of the freshly precipitated substance, or that an amount of it containing 1 gram of CuO would occupy 1·4 c.c.; yet this amount of precipitate, however long it may be left in the liquid out of which it has been precipitated, never agglomerates so as to occupy less than about 110 c.c., or eighty times the actual volume of the precipitate.

The precipitate, as has been mentioned, was dried by prolonged exposure over sodium hydroxide, but whether it had arrived at a constant weight, or not, was not determined, for the actual amount of water retained by it was immaterial for the immediate purposes; it may be accidental, therefore, though it is suggestive, that the $11{\cdot}746H_2O$ retained by it almost exactly corresponds with the equivalents of metallic oxides in the molecule, which amount to 11·64; as if these oxides were present as hydroxides.

About half this water is lost at 100°, although with extreme slowness, the precipitate changing from a full blue to green; it then contains $5{\cdot}098H_2O$. About $2H_2O$ more is lost at 150°, and it assumes an olive-green colour. At a low red heat all the water, as well as the SO_3 combined with the copper, is given off, the observed loss being 22·010 per cent., against a calculated loss of 22·122 per cent.

The Constitution of Water.

The fact that water of crystallisation, and the water of hydration in non-crystalline substances, has the same density as ice, is one which appears to be of the highest importance from the chemical and physico-chemical point of view, and it is remarkable that its significance has not hitherto attracted attention, for it seems to lead inevitably to the conclusion that solid water and liquid water must be different chemical compounds. The expansion occurring when water freezes is altogether phenomenal; there are very few substances that expand at all on solidification, and there is no substance, so far as we know, which exhibits an expansion at all comparable with that of water. It has been tacitly assumed up to the present that this expansion is due to the grouping together of the molecules, so as to form an hexagonal crystal; but it is impossible that this should be the real explanation, when the same expansion occurs on liquid water being converted into solid water of combination; for this does not consist of hexagonal ice crystals. It is not conceivable that amorphous substances, still less that crystalline substances belonging to any and every crystalline system, should enclose within them ice crystals belonging to the hexagonal system; nor can it be imagined that the solidified water will assume a crystalline form other than the hexagonal, to suit the diverse crystalline forms of hydrated salts. There is also, perhaps, a stronger argument in the fact that the minimum number of water molecules which could arrange themselves in a hexagon is greater than the number of water molecules existing in many hydrated salts; and polymerisation of the composite molecule will not help us out of this difficulty. The specific heat of water of crystallisation, just like the volume of such water, is identical with the specific heat of ice, and leads to the same conclusion.

If the expansion of water on solidifying cannot be explained by the grouping of its molecules, the only explanation possible is that it is due to a rearrangement of the constituent atoms; that solid water is a different chemical compound from liquid water ; if a molecule of the one is H–O–H, a molecule of the other is something else. That a chemical change occurs when water freezes is in itself strongly suggested by the magnitude of the energy changes accompanying the phenomenon ; for in spite of its apparently simple constitution, the heat of fusion of water is greater than that of any known substance.

The chemical change from the one H_2O molecule to the other, like other chemical changes, does not, in all probability, occur at one fixed temperature, but throughout a range of temperature, and, although the actual freezing point of water is a perfectly definite point, it is certain that the changes accompanying that freezing extend from many degrees above to many degrees below that point (the expansion of water, and the viscosity and regelation of ice may be instanced). Some molecules, therefore, such as those constituting solid water, are evidently present in liquid water at low, and probably at all, temperatures, and water must, therefore, be a mixture of (at least) two kinds of molecules, the relative proportions of which would vary with the temperature. The general regularity of the alteration in volume of water from 100° to even below 0° (Pickering, *Phil. Mag.*, 1890, [v], **30**, 399) indicates that the alteration of a contraction into an expansion, as the freezing point is approached, does not imply any sudden alteration in the changes occurring, but that whatever form of molecule is responsible for the expansion at low temperatures, this must be present, although in smaller proportions, at all temperatures. The altogether exceptional magnitude of the specific heat of water strongly supports the view that changes of a more fundamental character than a mere rise in temperature are occurring when water is heated.

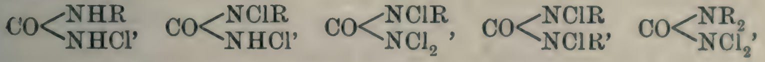
These considerations have an important bearing on suggestions recently made by Armstrong as to the complex nature of water (*Proc. Roy. Soc.*, 1908, **81**, *A*, 80).

HARPENDEN.

XVIII.—*Chlorine Derivatives of Substituted Carbamides.*

By Frederick Daniel Chattaway and Donald Frederick Sandys Wünsch.

The action of chlorine on carbamide should give rise to four distinct chloro-derivatives, namely, a monochloro-, a symmetrical and an unsymmetrical dichloro-, a trichloro-, and a tetrachloro-carbamide. Of these, only one dichlorocarbamide, without doubt the symmetrical compound, has so far been isolated. To ascertain whether halogen derivatives belonging to the other classes can exist, the action of chlorine on a number of substituted carbamides has been studied, and it has been shown that in them it is possible to replace by chlorine all the hydrogen attached to nitrogen, atom by atom. Compounds of the types:



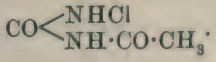
$$\mathrm{CO}\!\left<\begin{matrix}\mathrm{NHR}\\ \mathrm{NHCl}\end{matrix}\right., \quad \mathrm{CO}\!\left<\begin{matrix}\mathrm{NClR}\\ \mathrm{NHCl}\end{matrix}\right., \quad \mathrm{CO}\!\left<\begin{matrix}\mathrm{NClR}\\ \mathrm{NCl_2}\end{matrix}\right., \quad \mathrm{CO}\!\left<\begin{matrix}\mathrm{NClR}\\ \mathrm{NClR}\end{matrix}\right., \quad \mathrm{CO}\!\left<\begin{matrix}\mathrm{NR_2}\\ \mathrm{NCl_2}\end{matrix}\right.,$$

have been obtained, R being an acyl or an alkyl group.

The acyl monochlorocarbamides are crystalline solids, which are among the most stable chloroamino-compounds known. The acyl derivatives which contain more chlorine, and most of those which contain an alkyl group, are liquids which decompose on heating. Nearly all of the possible chloro-derivatives of acetyl-, benzoyl-, methyl-, *s*- and *as*-dimethyl-, ethyl-, *s*-diethyl-, and benzyl-carbamide have been prepared.

It is thus proved that, in a substituted carbamide, the replacement of one hydrogen atom by chlorine does not prevent the replacement by chlorine of a second hydrogen atom attached to the same nitrogen. There is every reason, therefore, to believe that the action of chlorine on carbamide itself gives rise to the other theoretically possible chloro-substitution products, and that these will be obtained when the conditions under which they can exist are ascertained, and when the difficulties attending their isolation have been overcome.

Acetylchlorocarbamide,



$$\mathrm{CO}\!\left<\begin{matrix}\mathrm{NHCl}\\ \mathrm{NH\cdot CO\cdot CH_3}\end{matrix}\right..$$

This compound separates in fine, needle-shaped crystals when a rapid stream of chlorine is passed into an aqueous solution of acetylcarbamide saturated at about 30—40°. It is obtained quite pure by collecting the crystals, washing them with a little water and then with chloroform, and drying them over phosphoric oxide in a vacuum. The chlorine in this and all the other compounds described in this paper was estimated by the method usually employed in analysing nitrogen halogen derivatives, by dissolving them in glacial acetic acid, adding excess of potassium iodide, and titrating the iodine liberated with sodium thiosulphate :

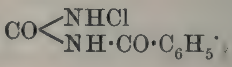
0·2496 liberated I = 36·6 c.c. *N*/10-I. Cl as $:\mathrm{NCl} = 25{\cdot}99$.
$C_3H_5O_2N_2Cl$ requires Cl as $:\mathrm{NCl} = 25{\cdot}97$ per cent.

Acetylchlorocarbamide crystallises from warm glacial acetic acid or from boiling chloroform, in both of which it is sparingly soluble, in slender, colourless plates with blunt ends and strong double refraction, which on collection form a felted mass. It melts when heated rapidly at 155—156°, at which temperature it decomposes and evolves gas ; the decomposition is accompanied by slight crackling explosions, probably due to the detonation of vapour of nitrogen chloride which is liberated in the decomposition.

When compared with dichlorocarbamide, acetylchlorocarbamide must be regarded as an extremely stable substance. It dissolves either in warm chloroform or warm glacial acetic acid without alteration, and can be kept for some days in a dry atmosphere without perceptible change ; it decomposes very slowly, however, with liberation of vapour of nitrogen chloride.

As in this compound only one of the three hydrogen atoms attached to nitrogen in acetylcarbamide is replaced by chlorine, this substitution might have been effected either in the amino- or in the acetylamino-group. Bearing in mind the circumstance that nitrogen chloride is evolved in the hydrolysis and decomposition of the compound, and that in the most easily isolated derivative of carbamide itself two hydrogen atoms only are exchanged for chlorine, it seems almost certain that it is one of the hydrogen atoms of the amino-group which is thus replaced.

Benzoylchlorocarbamide,



$$CO\Big\langle{}^{NHCl}_{NH\cdot CO\cdot C_6H_5}.$$

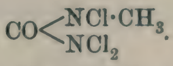
This compound is best prepared by passing a rapid stream of chlorine into a warm solution of benzoylcarbamide in glacial acetic acid until it is thoroughly saturated with chlorine. As the compound is more easily soluble in glacial acetic acid than the parent substance, it remains dissolved ; it is, however, precipitated in colourless, slender plates by diluting the cold solution, best with a saturated aqueous solution of chlorine. It is slightly soluble in warm chloroform, and can be recrystallised from this solvent, but is best crystallised from warm glacial acetic acid, in which it is fairly readily soluble and from which it separates, on cooling, in small, colourless, elongated plates ;

these show strong double refraction and straight extinction; when pressed together they form a lustrous, pearly mass:

0·3472 liberated I = 35·1 c.c. *N*/10-I. Cl as :NCl = 17·92.

$C_8H_7O_2N_2Cl$ requires Cl as :NCl = 17·85 per cent.

Benzoylchlorocarbamide melts and decomposes at about 157°, but the temperature varies somewhat with the rapidity of heating. Melting and decomposition are accompanied by the evolution of gas and by sharp crackling explosions, probably due, as in the case of the acetyl derivative, to the detonation of nitrogen chloride liberated in vapour when the compound decomposes.

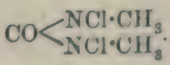
Methyltrichlorocarbamide,  $CO<\genfrac{}{}{0pt}{}{NCl\cdot CH_3}{NCl_2}$.

Although methylcarbamide is easily acted on by chlorine, which without doubt replaces the aminic hydrogens atom by atom, derivatives containing one or two atoms of chlorine have not so far been obtained, the oily liquid which separates when chlorine is led into a cooled aqueous solution of methylcarbamide consisting of the trichloro-derivative. After having been separated, washed with a little water, and dried over fused calcium chloride, it forms a fairly mobile, bright yellow-coloured liquid with an extraordinarily penetrating and irritating odour:

0·2947 liberated I = 99·1 c.c. *N*/10-I. Cl as :NCl = 59·6.

$C_2H_3ON_2Cl_3$ requires Cl as :NCl = 59·95 per cent.

Methyltrichlorocarbamide volatilises easily in a current of air, and slowly decomposes on standing, giving off bubbles of gas. When a few drops contained in a test-tube are heated rapidly in an oil-bath, decomposition occurs at about 70—80° with slight explosion, fumes of hydrogen chloride being given off and a white, solid residue left. It dissolves readily in water, giving a colourless solution having the strong pungent odour of the compound itself; on warming this solution, the methyltrichlorocarbamide is hydrolysed, nitrogen chloride, chloromethylamine, nitrogen, and carbon dioxide being evolved. On adding to it a concentrated solution of potassium hydroxide, a white, solid substance is formed, which almost at once decomposes violently with rapid evolution of gas.

s-*Dimethyldichlorocarbamide*,  $CO<\genfrac{}{}{0pt}{}{NCl\cdot CH_3}{NCl\cdot CH_3}$.

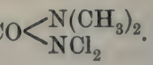
This separates as an oily liquid when chlorine is passed into a saturated aqueous solution of *s*-dimethylcarbamide as long as it is absorbed. It is best obtained pure by adding a little chloroform, in which the oily liquid readily dissolves, separating this chloroform solution, drying it by fused calcium chloride, and removing the chloroform in a stream of warm, dry air. *s*-Dimethyldichlorocarbamide is thus obtained as a colourless oily liquid with a sharp irritating odour:

0·2266 liberated I = 57·9 c.c. *N*/10-I. Cl as :NCl = 45·29.

$C_3H_6ON_2Cl_2$ requires Cl as :NCl = 45·16 per cent.

When heated, it decomposes, sometimes with a feeble explosion. When warmed with water, it is for the most part hydrolysed with liberation of chloromethylamine and formation of carbon dioxide.

as-*Dimethyldichlorocarbamide*,



$$CO<\begin{matrix}N(CH_3)_2\\NCl_2\end{matrix}.$$

This separates similarly as an oily liquid when *as*-dimethylcarbamide is dissolved in water and chlorine passed rapidly in to saturation, the solution meanwhile being well cooled. It was isolated as previously described by means of chloroform, and, after drying and volatilising the solvent, was obtained as a pale yellow oily liquid with a strong pungent odour:

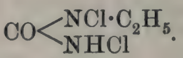
0·2438 liberated I = 61·2 c.c. *N*/10-I. Cl as :NCl = 44·49.

$C_3H_6ON_2Cl_2$ requires Cl as :NCl = 45·16 per cent.

The compound is very unstable, and, if kept, quickly decomposes, bubbles of gas and the vapour of nitrogen chloride escaping. When heated quickly it explodes feebly; on heating more slowly it decomposes rapidly, giving off gas and leaving behind a white, crystalline residue.

When warmed with water, it is hydrolysed; nitrogen and nitrogen chloride are evolved, and carbon dioxide and dimethylamine are produced.

Ethyldichlorocarbamide,



$$CO<\begin{matrix}NCl{\cdot}C_2H_5\\NHCl\end{matrix}.$$

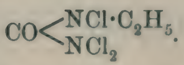
This separates when chlorine is passed into a cooled 20 per cent. aqueous solution of ethylcarbamide. It is a colourless, somewhat viscid liquid, which very readily decomposes when heated, giving off vapour of nitrogen chloride. When it is heated rapidly a feeble explosion results. This compound is very unstable, and quickly decomposes even when kept in a dry atmosphere:

0·2462 liberated I = 62·6 c.c. *N*/10-I. Cl as :NCl = 45·17.

$C_3H_6ON_2Cl_2$ requires Cl as :NCl = 45·16 per cent.

Ethyldichlorocarbamide dissolves fairly readily in water and becomes slowly hydrolysed; bubbles of nitrogen and carbon dioxide are evolved, and nitrogen chloride and chloroethylamine are given off. Hydrolysis becomes much more rapid if the solution is warmed.

Ethyltrichlorocarbamide,



$$CO<\begin{matrix}NCl\cdot C_2H_5\\ NCl_2\end{matrix}.$$

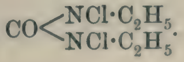
This compound is formed by the further action of chlorine on ethyldichlorocarbamide. It is best obtained by dissolving the dichloro-derivative in chloroform, covering it by about ten times its volume of water, and passing chlorine through the liquid for some considerable time, shaking continuously. The trichloro-derivative dissolves in the chloroform, and is obtained pure by washing the chloroform solution several times with water, drying over fused calcium chloride, and removing the chloroform in a current of warm air. Ethyltrichlorocarbamide is a fairly mobile, bright yellow liquid with a very penetrating odour, resembling that of the corresponding methyl derivative. Its vapour is very irritating to the eyes, and attacks the skin and mucous membranes. It volatilises moderately easily in a current of air. When heated cautiously it decomposes rapidly, but without explosion; if, however, the heating is sudden, as, for example, over a Bunsen flame, it may explode with great violence, a flash of light and white fumes being produced. This violent explosion may be due to the detonation of nitrogen chloride vapour which is given off as it decomposes:

0·2908 liberated I = 90·5 c.c. *N*/10-I. Cl as :NCl = 55·16.

$C_3H_5ON_2Cl_3$ requires Cl as :NCl = 55·56 per cent.

Ethyltrichlorocarbamide is far less soluble in water than the dichloro-compound. In presence of water it is hydrolysed, not, however, so readily as ethyldichlorocarbamide, nitrogen and carbon dioxide being evolved and nitrogen chloride and chloroethylamine liberated. With potassium hydroxide both it and the dichloro-compound are decomposed, nitrogen is evolved, a carbonate is formed, and an odour resembling that of a carbylamine is produced.

s-*Diethyldichlorocarbamide*,



$$CO<\begin{matrix}NCl\cdot C_2H_5\\ NCl\cdot C_2H_5\end{matrix}.$$

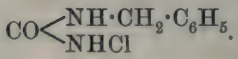
This separates when chlorine is passed into a cooled, saturated solution of *s*-diethylcarbamide. When isolated in the manner previously described, it forms a fairly mobile, colourless liquid with a penetrating odour. On heating it decomposes:

0·3427 liberated I = 73·5 c.c. *N*/10-I. Cl as :NCl = 38·01.

$C_5H_{10}ON_2Cl_2$ requires Cl as :NCl = 38·32 per cent.

It is hydrolysed by water, carbon dioxide and chloroethylamine being formed.

Benzylchlorocarbamide,



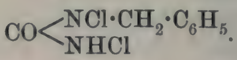
$$CO<\begin{matrix}NH\cdot CH_2\cdot C_6H_5\\ NHCl\end{matrix}.$$

When chlorine is passed into a saturated aqueous solution of benzylcarbamide, the liquid becomes turbid, and a colourless, oily substance separates. If the passage of the chlorine is not too long continued, this, after a short time, solidifies to a white, crystalline mass, consisting mainly of benzylchlorocarbamide. From this the monochloro-derivative can be obtained pure by pressing thoroughly between filter paper, washing with a little light petroleum, and drying over phosphoric oxide. It forms a white, crystalline solid, which melts and evolves gas at about 85—90°; decomposition begins, however, before the melting point is reached, and consequently the exact point at which the solid liquefies depends on the rate at which it is heated:

0·1332 liberated I = 15·1 c.c. *N*/10-I. Cl as ⁚NCl = 20·09.

$C_8H_9ON_2Cl$ requires Cl as ⁚NCl = 19·21 per cent.

Benzyldichlorocarbamide,



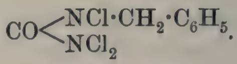
$$CO<\begin{matrix}NCl\cdot CH_2\cdot C_6H_5\\ NHCl\end{matrix}.$$

This compound is obtained by passing chlorine rapidly through a saturated solution of benzylcarbamide until the solid compound first produced liquefies. After separation by means of chloroform as previously described, it is obtained as a colourless, rather viscid liquid with the sharp irritating odour characteristic of all highly-substituted chlorocarbamides. It is very unstable, and if kept for a few hours decomposes, giving off nitrogen chloride and frothing from evolution of nitrogen. On slowly heating, it decomposes very rapidly, giving off white fumes and leaving behind a brown, viscid residue:

0·5395 liberated I = 97·3 c.c. *N*/10-I. Cl as ⁚NCl = 31·96.

$C_8H_8ON_2Cl_2$ requires Cl as ⁚NCl = 32·37 per cent.

Benzyltrichlorocarbamide,



$$CO<\begin{matrix}NCl\cdot CH_2\cdot C_6H_5\\ NCl_2\end{matrix}.$$

This compound is obtained from either of the previously-described benzylchlorocarbamide or from benzylcarbamide itself by the prolonged action of excess of chlorine. The procedure adopted was similar to that used in the preparation of ethyltrichlorocarbamide. Benzyltrichlorocarbamide is a bright yellow, fairly mobile liquid, which is moderately volatile in a current of air, and gives off highly irritating vapours. When heated it explodes feebly with a red, lurid flame, much black smoke and fumes of hydrogen chloride being produced.

It is very sparingly soluble in water, but readily so in chloroform or glacial acetic acid. It is rather more stable than benzyldichlorocarbamide, and can be kept for a few hours at a low temperature without apparent change:

0·2712 liberated I = 62·9 c.c. *N*/10-I. Cl as :NCl = 41·11.

$C_8H_7ON_2Cl_3$ requires Cl as :NCl = 41·965 per cent.

The reactions of these compounds are being investigated, and some progress has been made in the direction of isolating other chloro-derivatives of carbamide itself.

The authors desire to express their thanks to Professor Odling, who has placed a laboratory at their service.

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XIX.—*The Interaction of Hydrogen and Chlorine.*

By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON.

BUNSEN AND ROSCOE (*Phil. Trans.*, 1857, **147**, 390) state that the rate of union of hydrogen and chlorine in a mixture composed of equivalent quantities of the two gases is decreased from 100 to 9·7 by the addition of five parts of oxygen in a thousand, and that a similar although less marked effect is noticeable when either hydrogen or chlorine is added to the same mixture, three parts of hydrogen in a thousand reducing the rate of interaction from 100 to 37·8, and one part of chlorine in a hundred from 100 to 60.

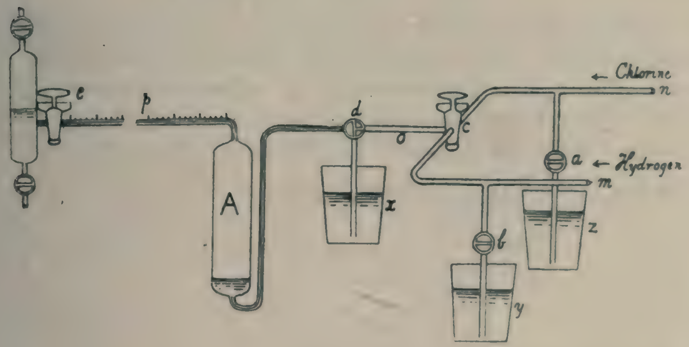
That the inhibitive influence of oxygen is considerable was established by Bunsen and Roscoe, and has subsequently received substantial confirmation; but the statement that the sensitiveness of electrolytic gas is appreciably reduced by the addition of a comparatively small volume of either of the constituent gases is still open to doubt.

We have made numerous attempts to measure the alleged inhibitive effects of small quantities both of hydrogen and of chlorine, but the experiments performed with this purpose in view have, until quite recently, furnished discrepant results, a circumstance which led us to conclude that the observed retardation was really due to impurities introduced with the hydrogen or chlorine. That this conclusion was correct is incontestably demonstrated by some experiments which we have lately performed. No appreciable retardation in the rate of interaction of hydrogen and chlorine is observable when a small volume of either hydrogen or chlorine in a state of purity is added to a mixture of the gases in equivalent proportions.

The hydrogen used by Bunsen and Roscoe was prepared by the electrolysis of dilute sulphuric acid and probably contained oxygen derived from the electrolyte, a source of error which we have succeeded in avoiding by using the hydrogen evolved from the cathode of the cell employed to obtain the electrolytic gas. In the electrolytic cell devised for the above-mentioned purpose there are two compartments separated by a porous diaphragm. Both compartments contain concentrated hydrochloric acid, in which graphite electrodes are immersed, one in each compartment. Each chamber is provided with a delivery tube, through which the evolved gas can be conducted. To destroy the ammonia and albuminoid impurities contained in the hydrochloric acid, an electric current is conducted through the cell first in one direction and then in the other, until the hydrochloric acid in both compartments contains chlorine gas in solution. The cell is then allowed to stand, preferably in a position where it will be exposed to daylight, for several days. The hydrochloric acid is afterwards electrolysed for twelve hours at least in order to displace every trace of oxygen. During the electrolysis, the hydrochloric acid in the anodic compartment becomes saturated with chlorine, and the chlorine in the cathodic compartment rapidly escapes with the evolved hydrogen, so that ultimately chlorine and hydrogen are evolved in equivalent proportions, whilst the separation of the two gases is almost complete. The cell is maintained at a constant temperature, and a current of 0·25 ampere is employed to electrolyse the acid contained in it.

The apparatus as disposed in an experiment is depicted in the accompanying diagram. The currents of chlorine and of hydrogen in the respective tubes n and m unite at the three-way tap, C, which is turned so that the tubes m and n communicate with the tube o. The three-way tap d is turned so as to admit the mixed gases to the insolation chamber of the actinometer, A. The latter contains about 5 c.c. of a dilute aqueous solution of chlorine, prepared by heating for some time at 100° a solution of chlorine in ammonia-free water. The gas escapes from the insolation chamber of the actinometer through the index tube, p. The electrolytic gas is passed through the actinometer for two hours at least. Then the tap d is turned so that the mixed gases escape through the potash solution in the beaker, n, and the actinometer is left in the dark for another hour before the sensitiveness of its contents is measured. The last precaution is taken in order to ensure the attainment of a state of complete equilibrium in the contents of the actinometer. The sensitiveness, or velocity of movement of the index in centimetres per minute, is then observed and recorded. In the making of this measurement a feeble light should be employed to bring about the combination of the chlorine and hydrogen, in order to reduce to a minimum the error due to delayed solution of the hydrogen chloride. To test for the absence of oxygen the mixed gases are passed again through the actinometer, this time for twenty minutes only, and a second measurement of the sensitiveness is made as before. If every trace of oxygen has been removed during the first filling of the actinometer then both measurements of the sensitiveness will furnish identical values. The experiment must not be started until the absence of oxygen in the electrolytic gas has been demonstrated.

To measure the effect of the addition of a small volume of hydrogen to the electrolytic gas on the sensitiveness, we proceed in the following way. The three-way taps, *C* and *d*, are adjusted so that hydrogen alone



passes through the tube *o* and escapes through the potash solution in *x*, the chlorine being conducted into the potash in *z*. When the chlorine in the tube *o* has been displaced, hydrogen is admitted to *A*, its volume being measured by the number of degrees through which the index is driven backwards, and then after the actinometer has remained in the dark for an hour the sensitiveness of the mixture is measured. The following results were obtained:

Percentage composition of mixture.		
Hydrogen.	Chlorine.	Sensitiveness.
50	50	11·92
52	48	11·90
53	47	11·70

The addition of a small volume of hydrogen to a mixture of hydrogen and chlorine in equivalent amounts has therefore an inappreciable effect on the sensitiveness.

It has been shown in a similar manner that the influence of a small excess of chlorine on the rate of formation of hydrogen chloride is negligible. One experiment is recorded below:

Percentage composition of mixture.		
Hydrogen.	Chlorine.	Sensitiveness.
50	50	17·3
49	51	17·6

The intensity of the light in the two experiments recorded above was different. There are accordingly only two known substances which will retard in a marked degree the interaction of hydrogen and chlorine, namely, nitrogen chloride and oxygen. Both these substances have a property in common. They will react with hydrogen chloride with the production of chlorine according to the equations:

$$4HCl + O_2 = 2Cl_2 + 2H_2O \text{ and}$$
$$NCl_3 + 3HCl = NH_3 + 3Cl_2.^*$$

It is possible that under certain conditions a reaction in which an element is formed will retard another reaction in which the same element is destroyed. The facts seem to indicate that such may be the case. We mention this conjecture merely because it has suggested experiments which are at present in progress.

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XX.—*Nitrogen Chloride.*

By David Leonard Chapman and Leonard Vodden.

The question of the true composition of nitrogen chloride possesses an especial interest for us on account of the observation made by C. H. Burgess and one of us that its vapour inhibits the photogenic interaction of chlorine and hydrogen. From the discrepant results of analyses carried out at different times over a period of almost a century on Dulong's explosive chloride, we were quite unable to decide whether this substance was the trichloride of nitrogen only, or a mixture (the composition of which depended on the mode of preparation) of this compound with compounds derived from ammonia by the partial displacement of hydrogen in the latter by chlorine. Unfortunately,

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* And possibly also according to the equations:

$$NCl_3 + HCl = NHCl_2 + Cl_2$$
$$NCl_3 + 2HCl = NH_2Cl + 2Cl_2.$$

no direct estimation of the hydrogen has ever been made. A sufficiently accurate idea of the degree of uncertainty at present attached to this question can be gained by reference being made to the following tabulated statement giving the formulæ calulated from the published analyses :

Authority.	Calculated formula.
Dulong (*Schweiggers J. Chem. Pharm.*, 1812, **8**, 32).	NCl_3.
Davy (*Phil. Trans.*, 1813, **103**, 1, 242).	NCl_4.
Porret, Wilson, and Kirk (*Gilb. Ann.*, 1814, **47**, 56, 59).	$NCl_{2\cdot 93}H_{1\cdot 09}$.
Bineau (*Ann. Chim. Phys.*, 1845, [iii], **15**, 82).	NCl_3.
Gladstone (*Quart. Journ. Chem. Soc.*, 1854, **7**, 51).	N_2Cl_5H.
Millon (*Ann. Chim. Phys.*, 1838, **69**, 75).	Found that the liquid contained hydrogen.
Gattermann (*Ber.*, 1888, **21**, 752).	For the substance prepared in the presence of excess of ammonium chloride : I, $NCl_{2\cdot 4}H_{0\cdot 6}$; II, $NCl_{1\cdot 78}H_{1\cdot 22}$; III, $NCl_{2\cdot 68}H_{0\cdot 32}$. For the substance after long exposure to chlorine, $NCl_{3\cdot 3}$.
Hentschel (*Ber.*, 1897, **30**, 192).	For the substance prepared in the presence of excess of ammonium chloride : I, $NCl_{3\cdot 00}$; II, $NCl_{2\cdot 95}$; III, $NCl_{3\cdot 02}$; IV, $NCl_{2\cdot 91}$.

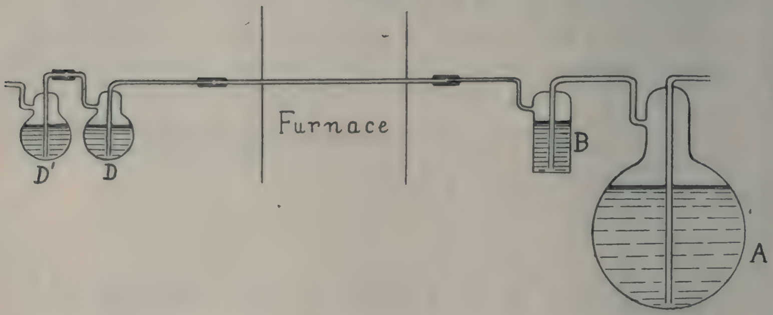
Half of the analyses indicate that the substance can contain an appreciable quantity of hydrogen ; of the modern observers, Gattermann, whose results were accepted for many years, found that the whole of the hydrogen in ammonia could only be replaced by chlorine after long treatment of the oil with the latter element ; but the more recent analyses of Hentschel are in entire disagreement with this view. The disputed point can only be satisfactorily settled by a direct estimation of the hydrogen. This we have accomplished, and we find that the content of hydrogen is very small indeed, although the nitrogen chloride examined by us was prepared in the presence of a large excess of ammonium chloride. An independent estimation of the ratio of nitrogen to chlorine has confirmed this result.

Analysis of Nitrogen Chloride.

Estimation of the Hydrogen.—Chlorine gas was passed into a concentrated solution of ammonium chloride, and the aqueous solution of nitrogen chloride thus obtained was introduced into the flask *A* (Fig. 1).

A current of nitrogen carefully purified from oxygen was then passed through the solution, and the mixture of nitrogen and vapour of nitrogen chloride, after being dried, was passed through a quartz tube heated to the highest temperature attainable with a Fletcher's fire-clay combustion furnace. The heated portion of the quartz tube was enclosed in a tube of glazed Berlin porcelain to prevent the furnace gases from coming into contact with the quartz, this material being pervious to hydrogen at high temperatures. Since in a quartz tube heated in the manner described, nitrogen chloride is completely destroyed, any hydrogen present in the vapour would appear as hydrogen chloride in the issuing gases. The wash-bottles *D* and *D′*, containing a neutral solution of potassium iodide, were attached to the end of the quartz tube after all the air in the apparatus had been displaced by nitrogen. The iodine liberated from the potassium iodide and the acquired acidity of the solution were, of course, respectively proportional to the hydrogen and available chlorine in the vapour. When a convenient quantity of iodine had been liberated—the depth of colour assumed by the solution being taken as a guide—the wash-bottles were detached, and their contents titrated with an *N*/10-

FIG. 1.



solution of sodium thiosulphate, the acidity being subsequently estimated with $N/100$-potassium hydroxide, using phenolphthalein as indicator. The following amounts of the standard solutions were required:

30 c.c. of $N/10$-sodium thiosulphate.
0·5 c.c. of $N/100$-potassium hydroxide.

Whence we conclude that there is less than one atom of hydrogen to every three hundred atoms of chlorine in nitrogen chloride prepared in the presence of a concentrated solution of ammonium chloride.

A similar result was obtained when the vapour of nitrogen chloride, together with the small amount of nitrogen resulting from its decomposition in the solution, was drawn through the heated quartz tube and then through the potassium iodide solution with a Sprengel pump, the apparatus having been suitably modified for the purpose.

Estimation of the Ratio of Nitrogen to Chlorine.—The ratio of nitrogen to available chlorine was determined in a solution of nitrogen chloride in carbon tetrachloride, in which solvent the nitrogen chloride is remarkably stable.

A solution of nitrogen chloride in pure carbon tetrachloride was prepared in the following way. About 150 c.c. of carbon tetrachloride in a separating funnel were covered with a layer of a concentrated aqueous solution of recrystallised ammonium chloride. Chlorine gas was passed into the solution of ammonium chloride, the resulting nitrogen chloride being dissolved in the carbon tetrachloride by shaking the latter vigorously with the aqueous solution. The operation was repeated several times until the carbon tetrachloride had assumed a bright yellow colour.* The heavy solution of nitrogen chloride in carbon tetrachloride was then separated from the aqueous ammonium chloride and washed four or five times with distilled water. The analysis was performed with the apparatus depicted in Fig. 2. The yellow solution of nitrogen chloride was introduced into the funnel *B* after the air in the flask *A* (which contained a known volume of a standard solution of sodium arsenite) and in the rest of the apparatus had been completely removed by a Sprengel pump, not shown in the figure. When the taps *m* and *n* had been closed, most of the solution of the chloride of nitrogen in *B* was cautiously admitted into the flask *A*. The yellow solution was shaken with the standard sodium arsenite until the former had completely lost its colour, the flexible rubber joint at *B* permitted of this being done. The small amount of nitrogen evolved during the operation, together with some carbon dioxide derived from the sodium hydrogen carbonate in the standard arsenite solution, was pumped out of the apparatus through an acidified solution of potassium iodide contained in the wash-bottle *C*, and collected. That the nitrogen chloride had been completely reduced by the sodium arsenite was proved by the circumstance that the potassium iodide in *C* was not discoloured while the gases were being withdrawn. The gas collected at the pump was measured and analysed, an allowance being made for the vapour pressure of carbon tetrachloride; it was found to contain, in addition to nitrogen and carbon dioxide, a minute trace of oxygen, which was ignored in the final calculation, since its amount was so small that a correction made for it on any conceivable hypothesis to account for its presence would have been negligible in comparison with the other errors of experiment. The residual arsenite and the ammonia[*] contained in the flask *A* were also estimated. From the amounts of arsenite destroyed and ammonia and nitrogen produced, the formula of nitrogen chloride was calculated on the assumption that chlorine and nitrogen are the only components of that compound. Three experiments furnished results, from which the following formulæ were calculated:

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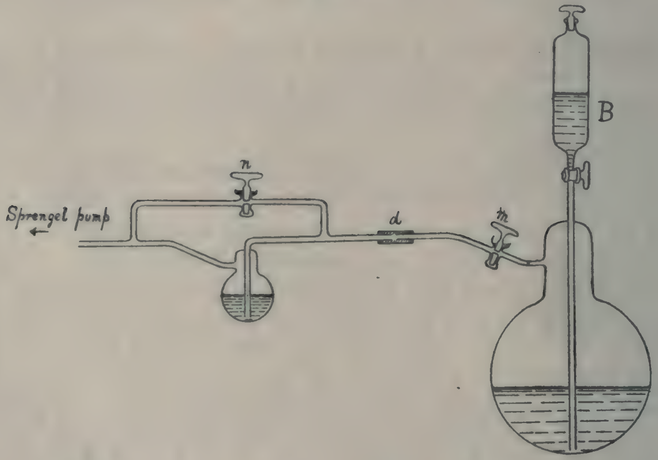
* The tint of a solution of nitrogen chloride in carbon tetrachloride is indistinguishable from that of a solution of chlorine in the same solvent.

FIG. 2.



$$\text{I. } NCl_{3\cdot03}. \qquad \text{II. } NCl_{3\cdot06}. \qquad \text{III. } NCl_{3\cdot06}.$$

From the results of two earlier experiments, in which a solution of potassium iodide was employed to decompose the nitrogen chloride in the place of a standard arsenite solution, the following formulæ were calculated:

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[*] Nitrogen chloride is reduced by sodium arsenite almost entirely to ammonia, whereas a relatively large proportion of nitrogen results from its reduction by an acidified solution of potassium iodide. In the latter case, the liberated iodine appears to facilitate the direct decomposition of the nitrogen chloride into its constituent elements.

$$\text{I. } NCl_{3\cdot 14}. \qquad \text{II. } NCl_{2\cdot 84}.$$

From the above results we conclude that nitrogen chloride prepared by the action of chlorine on a neutral solution of ammonium chloride contains little, if any, hydrogen, and that the nitrogen and chlorine are present in the proportion of one atomic weight of nitrogen to three of chlorine.

The Hydrolysis of Nitrogen Chloride.

Seliwanoff (*Ber.*, 1894, **27**, 1012) has shown that several facts relating to nitrogen chloride can be more clearly understood if it is postulated that in aqueous solution the substance is hydrolysed according to the equation:

$$NCl_3 + 3H_2O \rightleftharpoons NH_3 + 3HClO.$$

Thus, the extreme ease with which nitrogen chloride is reduced to ammonia receives an intelligible explanation, and the fact that the apparent solubility of nitrogen chloride in aqueous hydrogen chloride is greater than in sulphuric acid or in water is satisfactorily explained, for hypochlorous acid, one of the products of hydrolysis, is destroyed by hydrogen chloride, but is not affected by sulphuric acid. So far, the evidence adduced in support of the view that nitrogen chloride is hydrolysed in solution according to the above equation has been of an indirect character. We have accordingly carried out a simple experiment with the object of demonstrating the formation of ammonium salts from nitrogen chloride by hydrolysis alone. The experiment was conducted in the following way. A concentrated solution of nitrogen chloride in carbon tetrachloride was shaken in a flask of moderately concentrated hydrochloric acid, whereby, if Seliwanoff's view is right, ammonium chloride and chlorine should be formed according to the following equations:

$$\begin{aligned} NCl_3 + 3H_2O &\rightleftharpoons NH_3 + 3HClO \\ HClO + HCl &\rightleftharpoons Cl_2 + H_2O \\ NH_3 + HCl &\rightleftharpoons NH_4Cl \end{aligned}$$

and the chlorine, being soluble in carbon tetrachloride, should be removed and an excess of ammonium chloride left in the aqueous layer. The carbon tetrachloride was then separated, and the nitrogen chloride removed from the aqueous solution at the pump. The acid solution was next rendered alkaline by the addition of ammonia-free potassium hydroxide, and distilled. The distillate contained a considerable quantity of ammonia the presence of ammonium chloride in the aqueous layer being thereby demonstrated.

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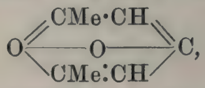
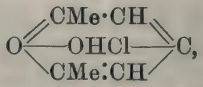
XXI.—*The Relation between Absorption Spectra and Chemical Constitution. Part XIII. Some Pyrones and Allied Compounds.*

By Edward Charles Cyril Baly, John Norman Collie, and Herbert Edmeston Watson.

The question of the constitution of the pyrones and their derivatives has been discussed at considerable length by Feist, Claisen, and Collie, but only from a chemical standpoint. The subject is a difficult one, being complicated by the possible presence of quadrivalent oxygen, but for this reason presents a greater interest. The only physical measurements made up to the present are those of the molecular refractions by Miss Homfray (Trans., 1905, **87**, 1443) in a paper which is a very valuable contribution to the literature dealing with these compounds. In every compound examined, Miss Homfray obtained values for the molecular refractivity which were considerably higher than the additive values calculated from the usually accepted molecular formulæ. This excess value was attributed by the author to the presence of quadrivalent oxygen, and formulæ were given to the compounds examined involving the presence of one or more atoms of quadrivalent oxygen. For example, the formula of dimethylpyrone put forward by Collie (Trans., 1904, **85**, 973),



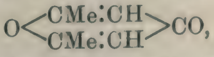
was adopted—a formula which satisfies in a very marked way the abnormal properties of this compound, as for example, its inability to form an oxime or phenylhydrazone. The hydrochloride of dimethylpyrone would then be represented by the formula



which agrees extremely well with the molecular refractivity, involving, as it does, two quadrivalent oxygen atoms. Using the above formula for dimethylpyrone, the atomic refractivity of quadrivalent oxygen was found by Miss Homfray to be 2·65, and the value obtained from the above formula of the hydrochloride was 2·79. These two values are in very good agreement, and, moreover, the increase in refractivity incurred in passing from the base to its salt is of very considerable importance, as will be shown below. Since the appearance of Miss Homfray's paper, a considerable amount of work has been carried out by Brühl (Trans., 1907, **91**, 115) and others, dealing with the influence of contiguous double linkings on molecular refractivity, the presence of these contiguous double linkings always giving an exalted value for the refractivity, that is to say, a value which is greater than the purely additive value as obtained from the simple graphic formula of the compound. It would appear that some of the refractivities obtained by Miss Homfray for the other compounds examined by her are subject to a correction for this reason. It is impossible to estimate the magnitude of this correction in the light of our present knowledge, but it is not improbable that the exalted values of refractivity in many cases are partly due to this cause and are not entirely to be attributed to the presence of quadrivalent oxygen.

It was thought that independent evidence of the constitution of dimethylpyrone and the allied compounds might be obtained from an examination of their absorption spectra, and consequently we have examined all the available compounds of this type; the present paper contains an account of the results obtained in the more important cases.

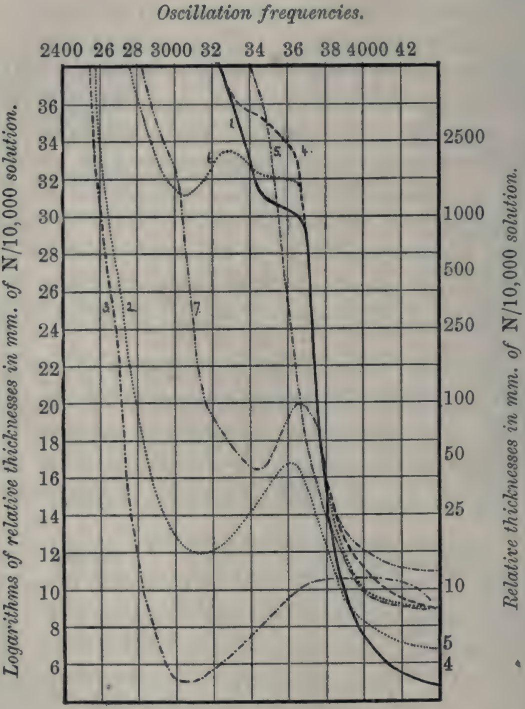
The first compounds examined were 4-pyrone, 2 : 6-dimethyl-4-pyrone, and 2 : 3 : 5 : 6-tetramethyl-4-pyrone, and it was found that the absorption curves of the three are essentially the same. The absorption of the first two compounds in alcoholic solution is shown in Fig. 1, curves 1 and 4, the curve of tetramethylpyrone being so similar to that of dimethylpyrone as not to justify its reproduction. It is evident that not one of these compounds shows an absorption band, there being only a somewhat rapid extension of the curves at higher concentrations. The addition of hydrogen chloride to the alcoholic solution causes this extension to disappear, as can be seen from curve 5, Fig. 1, which shows the absorption of dimethylpyrone in presence of considerable excess (50 equivalents) of hydrochloric acid. The small amount of absorption exhibited by these curves cannot in any way be reconciled with the ordinary pyrone formula, namely,



$$\mathrm{O}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CMe{:}CH}\end{matrix}>\mathrm{CO},$$

for not only is there a carbonyl group situated between two ethylenic double linkings, but there is also the added effect of the unsaturated oxygen atom in the ring. On the other hand, the bridged-ring structure put forward by Collie (*loc. cit.*) would naturally give rise to the small amount of general absorption we have observed. The slight extension on the absorption curve would then arise from the play of forces between the residual affinity of the central or bridged oxygen and the three double linkings of the ring. This view is supported by the fact that in the presence of hydrogen chloride this sudden extension on the absorption curve is entirely eliminated.

FIG. 1.

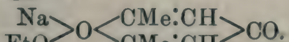


1. 4-*Pyrone in alcohol.*
2. ,, + 1 *equivalent of* NaOEt.
3. ,, + 60 *equivalents of* NaOEt.
4. *Dimethylpyrone in alcohol.*
5. ,, + *great excess of* HCl.
6. ,, + 87 *equivalents of* NaOEt.
7. ,, *in water* + 100 *equivalents of* NaOH.

A very significant fact referred to above is that the molecular refractivity of the hydrochloride of dimethylpyrone has an even greater exalted value than the free base. If, as might possibly be suggested, the exalted values given by the free base were due to some arrangement of contiguous double linkings, it would be impossible to conceive how this could be further exalted by the removal of some of the residual affinity consequent on the addition of one molecule of hydrogen chloride.

The evidence, therefore, is very strongly in favour of the bridged-ring formula for the pyrones, since this formula satisfies the values obtained with the refractometer and the spectroscope, and also is supported by their chemical behaviour.

A very marked change in the absorption of the pyrones is manifested on the addition of sodium ethoxide to their solutions in alcohol. Curves 2 and 3, Fig. 1, show the absorption of pyrone in presence of one and sixty equivalents of sodium ethoxide respectively. A well-marked absorption band is now produced with the one equivalent and intensified with the sixty equivalents. Very similar results are produced with dimethylpyrone, only in this case a greater relative concentration of sodium ethoxide is required (Fig. 1, curve 6). The curve in the latter case is very strikingly similar to that given by γ-lutidone in presence of hydrogen chloride (Baker and Baly, Trans., 1907, **91**, 1122), and, moreover, the chemical evidence shows that an additive compound of dimethylpyrone and sodium ethoxide is formed (Collie and Steele, Trans., 1900, **77**, 970). The analogy to lutidone hydrochloride suggests at once that the additive compound is to be represented by

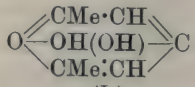


$\begin{matrix}\mathrm{Na}\\ \mathrm{EtO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CMe{:}CH}\end{matrix}\!>\!\mathrm{CO}.$

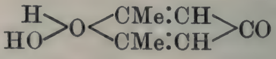
As was pointed out in the previous paper, lutidone hydrochloride is very similar in its absorption to phorone, where a carbonyl group is situated between two double linkings, so that the spectroscopic evidence is in favour of the addition of the sodium ethoxide to dimethylpyrone as in the above formula. There is thus a very striking difference in the addition of hydrogen chloride and of sodium ethoxide to dimethylpyrone, for the former unites with the oxygen atom in the bridge, whilst in the latter case, the addition takes place to the oxygen atom in the ring, the bridge being first ruptured.

The effect of the addition of alkali to an aqueous solution of dimethylpyrone is entirely different from that obtained in alcoholic solution, as can be seen from curve 7, Fig. 1. It is well known that the addition of alkali to an aqueous solution of dimethylpyrone tends to give the sodium salt of diacetylacetone, and, indeed, the absorption curve obtained approximates to that of diacetylacetone in aqueous alkali (Fig. 2, lower curve 2), so that no doubt a considerable quantity of this substance is formed.

The results obtained from the spectroscopic examination of diacetylacetone have proved somewhat complex, owing to the various forms in which this substance might exist. It is evident from its empirical formula that it might exist either as a hydrate of dimethylpyrone or as an open-chain compound. There are thus three different possibilities as follows:



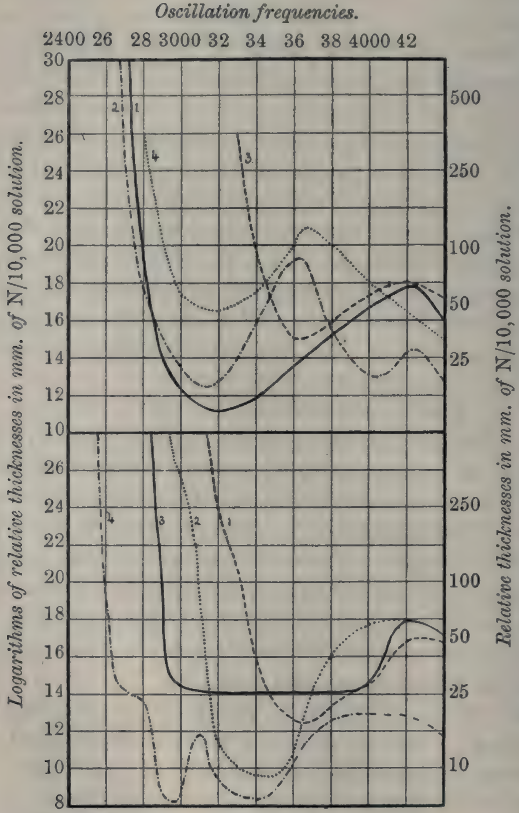
(I.)



(II.)

$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_3$
(III.)

FIG. 2.



Upper curves—1. *Dimethylpyrone: ethyl alcohol compound.*
2. ,, ,, ,, + 2 *equivalents of* NaOEt.
3. *Pyromeconic acid.*
4. ,, ,, + 4 *equivalents of* NaOEt.

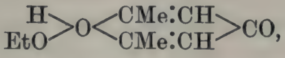
Lower curves—1. *Diacetylacetone in water.*
2. ,, ,, + 10 *equivalents of* NaOH.
3. ,, *in alcohol.*
4. ,, ,, + 9 ,, NaOEt.

and, further, of these, (III) might exist in one of the possible enolic forms.

Now the absorption curves of diacetylacetone in aqueous and alcoholic solutions (Fig. 2, lower curves 1 and 3) are entirely different from one another, but whatever may be the final interpretation, there is no doubt that formula (I) above must be ruled out of court, for neither of the two curves bears the slightest resemblance to that of dimethylpyrone hydrochloride. We are therefore left with the two forms (II) and (III), and in order to test the validity of (III), or rather the dynamic equilibrium of the ketonic and enolic forms, we have examined the absorption spectrum of tetra-acetylethane, which possesses an analogous structure to (III). The absorption of the latter compound is shown on Fig. 3, lower curves 3 and 4, in neutral and alkaline solutions respectively. The type of absorption closely resembles that of diacetylacetone in aqueous solution, and, indeed, the absorption of both these compounds is of the keto-enolic type, as exemplified by acetylacetone, etc. (Baly and Desch, Trans., 1904, **85**, 1029). There is therefore every justification for the conclusion that diacetylacetone in aqueous solution exists in the open-chain configuration, and that it is a dynamic equilibrium mixture of the ketonic and enolic forms.

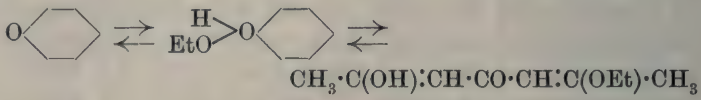
The case is different when the compound is dissolved in alcohol, for the absorption curve shows a most exceptionally broad band. It is, however, of some importance to note that this band covers the region occupied by the band given by an alcoholic solution of dimethylpyrone in presence of sodium ethoxide and the band of diacetylacetone in aqueous solution. Now it is clear that if the diacetylacetone had the form (II), its absorption would conform more or less to that of pyrone in presence of alcoholic sodium ethoxide; the absorption, however, is compounded of that of the open-chain formula and of that of pyrone in alcoholic sodium ethoxide. For this reason it appears certain that diacetylacetone in alcoholic solution exists in *both* forms, (II) and (III). This conclusion is borne out by the fact that under certain conditions the alcoholic solution shows the broad absorption band subdivided into two, one due to form (II) and the other due to form (III). The addition of sodium ethoxide to the alcoholic solution of dimethylpyrone still further supports this conclusion, for two absorption bands are exhibited (Fig. 2, lower curve 4), one almost the same as that of dimethylpyrone in presence of alcoholic sodium ethoxide (Fig. 1, curve 6), and the other the same as diacetylacetone in presence of aqueous alkali (Fig. 2, lower curve 2).

In Fig. 2, upper curves 1 and 2, is shown the absorption of the alcohol compound of dimethylpyrone in neutral and alkaline alcoholic solution respectively. A comparison of the latter with Fig. 1, curve 6, shows at once that at the strength employed (*N*/100), 87 equivalents of sodium ethoxide only partly convert the dimethylpyrone into the additive compound. From analogy to diacetylacetone, the formula of the alcohol compound of dimethylpyrone would appear to be

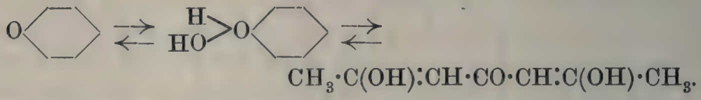


$$\begin{matrix}\mathrm{H}\\\mathrm{EtO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{CMe{:}CH}\\\mathrm{CMe{:}CH}\end{matrix}\!>\!\mathrm{CO},$$

and is therefore the monomethyl ether of diacetylacetone. It is interesting to compare the readiness with which this compound loses alcohol and diacetylacetone loses water. Whereas, in the former case, the molecule of alcohol is removed with the greatest of ease, diacetylacetone only loses its water with difficulty. This may be represented in another way by comparing the two reversible processes:

(*a*)


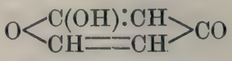
$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OEt){\cdot}CH_3$

(*b*)


$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_3$.

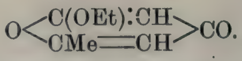
In (*a*) there is no tendency for the open-chain compound to be formed, but the intermediary compound prefers to pass into the pyrone; in (*b*), on the other hand, the open-chain compound is the most favoured in aqueous solution, and in alcoholic solution there is present some of the intermediary compound, probably in equilibrium with the open-chain form. The tendency is for the intermediary compound to pass into the open-chain; therefore it will only lose water with difficulty to give the pyrone.

Two derivatives of pyrone may next be dealt with, namely, pyromeconic acid and triacetic lactone, the absorption spectra of which are shown on the upper portions of Figs. 2 and 3 Pyromeconic acid (2-hydroxy-4-pyrone) in neutral alcoholic solution (Fig. 2, upper curve 3) is very interesting, for it exhibits a shallow absorption band which must arise from the influence of the hydroxyl group. An almost identical curve is given by triacetic lactone ethyl ether (Fig. 3, upper curve 3), showing that these two compounds possess an analogous structure. The head of the absorption band in each case is at about $^1/\lambda = 3000$, and therefore it is not possible that the conjugate linking occurs; in other words, their structure cannot be represented by the two formulæ:



$$\mathrm{O}\!<\!\begin{matrix}\mathrm{C(OH){:}CH}\\\mathrm{CH{=\!=}CH}\end{matrix}\!>\!\mathrm{CO}$$

Pyromeconic acid.

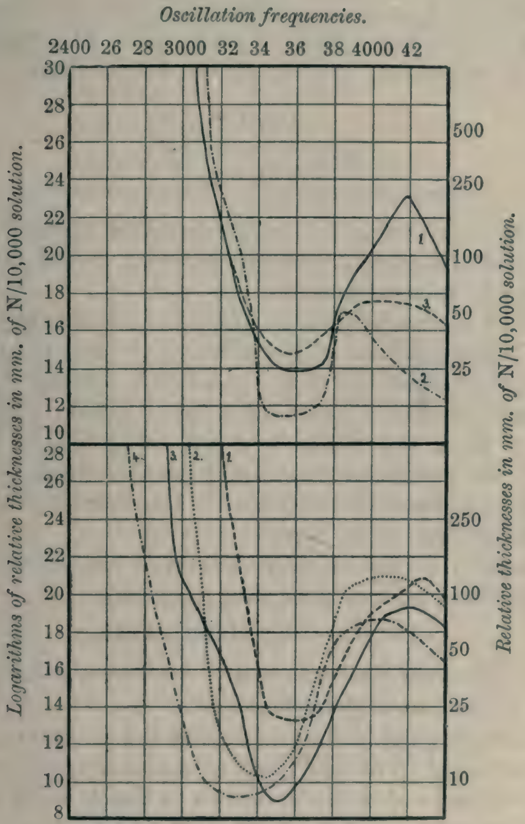


$$\mathrm{O}\!<\!\begin{matrix}\mathrm{C(OEt){:}CH}\\\mathrm{CMe{=\!=}CH}\end{matrix}\!>\!\mathrm{CO}.$$

Triacetic lactone ethyl ether.

Doubtless the bridged ring is also present in each case, and therefore the absorption band is due to the influence of the hydroxylic oxygen in each case. The addition of sodium ethoxide to the solution of pyromeconic acid produces an effect quite analogous to that observed with 4-pyrone itself. A similar additive compound is formed with the rupture of the bridge, with the result that the absorption curve obtained (Fig. 2, upper curve 4) is almost identical with that of the additive compound of pyrone and sodium ethoxide (Fig. 1, curve

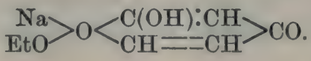
FIG. 3.



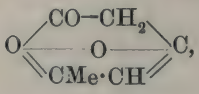
Upper curves—1. *Triacetic lactone.*
2. ,, ,, + 5 *equivalents of* NaOEt.
3. ,, ,, *Ethyl ether.*

Lower curves—1. *Ethyl ester of triacetic acid.*
2. ,, ,, + 5 *equivalents of* NaOEt.
3. *Tetra-acetylethane.*
4. ,, + 10 *equivalents of* NaOEt.

2). The absorption band is now produced by the contiguous double linkings, as expressed in the formula:



Triacetic lactone, on the other hand, has not the same structure as its ethyl ether, for a much deeper absorption band is produced (Fig. 3, upper curve 1). This difference, however, is in all probability to be explained by the lactone existing in the ketonic form,



the absorption band being due to the presence of some enol-ketonic tautomerism as in the case of camphor, to which, indeed, the absorption spectrum closely approximates.

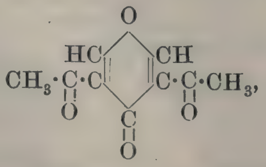
The addition of a small quantity of sodium ethoxide to the alcoholic solution of triacetic lactone is only sufficient to form the sodium salt, with no essential alteration in the absorption spectrum. As in the case of dimethylpyrone, a small quantity of sodium ethoxide is not sufficient to break the bridge with the formation of the additive compound. The presence of the methyl group restrains the formation of the additive compound in both cases. The discussion of this point may be reserved until later.

The absorption curves of ethyl triacetate are shown in Fig. 3, lower curves 1 and 2; this open-chain compound,

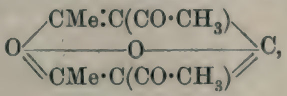
$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et,$$

exhibits an absorption similar to that of tetra-acetylethane and of the open-chain form of diacetylacetone.

A very striking proof of the existence of the bridged-ring structure of the pyrones is to be found in the case of diacetyldimethylpyrone, the absorption curve of which is shown in Fig. 4, curve 5. There is only slight general absorption, which is entirely incompatible with the ordinary formula:

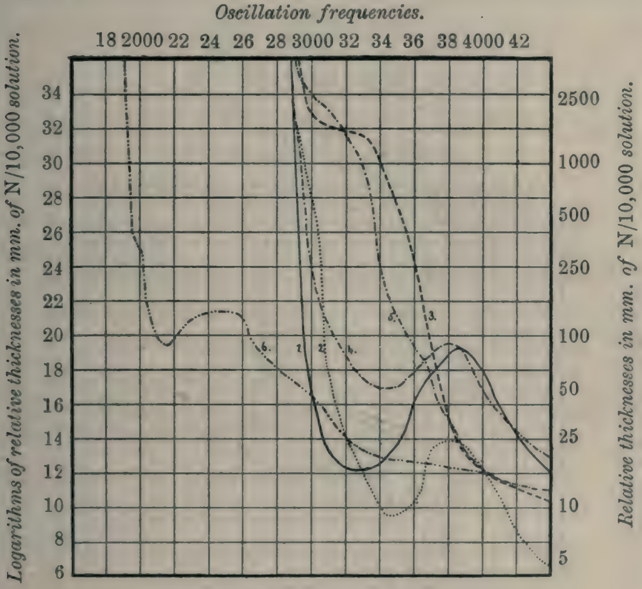


which possesses no fewer than five contiguous double linkings. If these linkings had free play, the compound would undoubtedly be coloured yellow and exhibit very strong absorption. The bridged-ring form is, however, free from this objection, as may readily be seen:

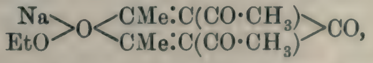


or the structure is comparable with a benzenoid compound, where, as is well known, the benzenoid dynamic activity is restrained by the substitution by acetyl and other electronegative groups. In this case, as in the other pyrones, the ring is ruptured on the addition of sodium ethoxide, a yellow compound being formed, the absorption of which is shown in Fig. 4, curve 6. As is evident from the formula:

FIG. 4.



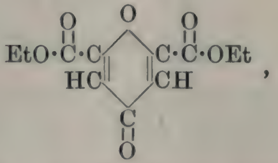
1. *Dehydracetic acid.*
2. ,, ,, +10 *equivalents of* NaOEt.
3. *Dimethylpyronecarboxylic acid.*
4. iso*Dehydracetic acid.*
5. *Diacetyldimethylpyrone.*
6. ,, +2 *equivalents of* NaOEt.



$$\begin{matrix} Na \\ EtO \end{matrix}\!>\!O\!<\!\begin{matrix} CMe\colon C(CO\cdot CH_3) \\ CMe\colon C(CO\cdot CH_3) \end{matrix}\!>\!CO,$$

the double linkings have now free play, with the formation of an absorption band as high up the spectrum as $1/\lambda = 2180$.

Quite similar arguments are applicable to chelidonic acid and its ethyl ester, for the absorption of these compounds in alcoholic solution (curve 1, Fig. 5) is quite impossible if the structure were represented by



and, as in the case of diacetyldimethylpyrone, the bridged-ring structure must be present in order to account for there being only small general absorption. The formula may therefore be written

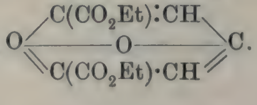
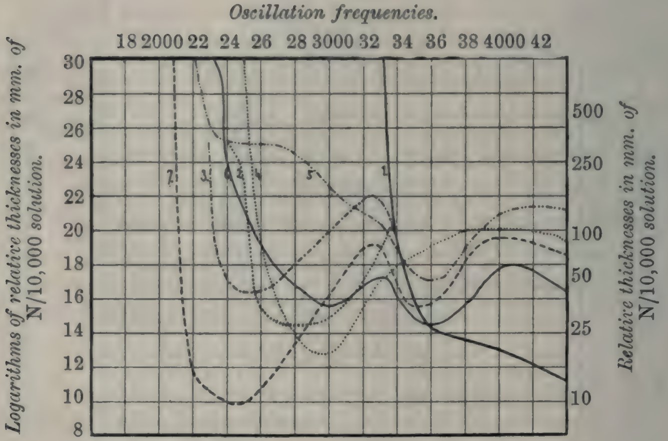


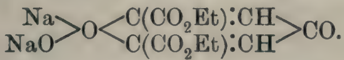
Fig. 5.



1. *Chelidonic ethyl ester.*
2. ,, ,, *in dry alcohol* + 100 *equivalents of* NaOEt.
3. ,, *acid* + 100 *equivalents of* NaOH *in water.*
4. *Xanthochelidonic ethyl ester in anhydrous chloroform.*
5. ,, ,, *in water.*
6. ,, ,, *in alcohol.*
7. ,, ,, ,, + 100 *equivalents of* NaOEt.

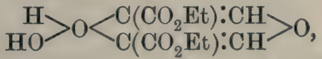
The addition of sodium ethoxide to the alcoholic solution, or of sodium hydroxide to the aqueous solution, as in the previous cases, forms a yellow additive compound with the consequent rupture of the bridge, so that there is every possibility for the free play of forces between the five contiguous double linkings (Fig. 5, curves 2 and 3).

Ethyl xanthochelidonate, the empirical formula of which corresponds with an additive compound of ethyl chelidonate and water, naturally exhibits very considerable absorption, since the bridged structure is no longer possible, and generally speaking the five contiguous linkings have free play. There is, however, very considerable difference in the absorption of this compound according to the nature of the solvent. In perfectly dry chloroform or ether, the substance forms a colourless solution, and the absorption exhibited is shown in Fig. 5, curve 4, there being present one absorption band with its head at about $^{1}/\lambda = 3000$. The addition of the slightest trace of water causes the solution to become intensely yellow, and since the amount of water is far less than is necessary to form an additive compound, this must be due to an isomeric change. On the other hand, the solution in alcohol in the presence of sodium ethoxide shows two absorption bands, one at $^{1}/\lambda = 2450$ and the other at $^{1}/\lambda = 3500$. This latter spectrum is quite analogous to that of ethyl chelidonate as obtained in aqueous alkaline solution, and would appear to be due to the sodium compound of the ester,



$$\begin{matrix}\mathrm{Na}\\ \mathrm{NaO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{C(CO_2Et){:}CH}\\ \mathrm{C(CO_2Et){:}CH}\end{matrix}\!>\!\mathrm{CO}.$$

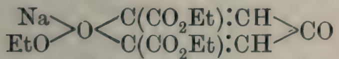
For this reason we are inclined to the view that ethyl xanthochelidonate in anhydrous chloroform or ether exists in the open-chain form, $\mathrm{CO_2Et{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Et}$, an explanation which might also account for the abnormally high values of the refractivity found by Miss Homfray for this compound in the former solvent. On these grounds the absorption results obtained with solutions in alcohol and in water (Fig. 5, curves 6 and 5) would be due to mixtures of the two forms, the closed ring,



$$\begin{matrix}\mathrm{H}\\ \mathrm{HO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{C(CO_2Et){:}CH}\\ \mathrm{C(CO_2Et){:}CH}\end{matrix}\!>\!\mathrm{O},$$

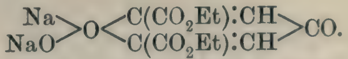
and the open chain.

A comparison of ethyl chelidonate and ethyl xanthochelidonate and their absorption spectra may be made, for the formulæ of the additive compounds may be written as follows:



$$\begin{matrix}\mathrm{Na}\\ \mathrm{EtO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{C(CO_2Et){:}CH}\\ \mathrm{C(CO_2Et){:}CH}\end{matrix}\!>\!\mathrm{CO}$$

Ethyl chelidonate in alcohol with sodium ethoxide.
(I.)

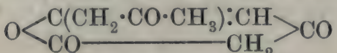


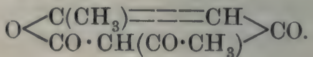
$$\begin{matrix}\mathrm{Na}\\ \mathrm{NaO}\end{matrix}\!>\!\mathrm{O}\!<\!\begin{matrix}\mathrm{C(CO_2Et){:}CH}\\ \mathrm{C(CO_2Et){:}CH}\end{matrix}\!>\!\mathrm{CO}.$$

Ethyl xanthochelidonate in alcohol with sodium ethoxide.
(II.)

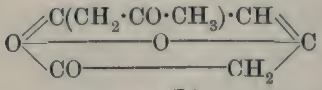
The two compounds differ merely by the replacement of the ethyl group in (I) by sodium in (II). That these compounds would differ in their absorption follows from a comparison of the esters and sodium salts of the unsaturated aromatic acids (Baly and Schaefer, Trans., 1908, **93**, 1808), and their spectra are shown in Fig. 5, curves 2 and 7 respectively. The addition of sodium hydroxide to a solution of chelidonic acid would tend to give substance (II) above; this is in agreement with the absorption obtained, as shown in Fig. 5, curve 3, which is very similar to curve 7, the slight difference being due no doubt to the fact that the acid was used in place of the ester.

We have also examined the absorption spectrum of dehydracetic acid, *iso*dehydracetic acid, and dimethylpyronecarboxylic acid. The curves for the first-named substance are shown in Fig. 4 (curves 1 and 2), and it may be seen at once that the addition of sodium ethoxide shifts the band towards the shorter wave-lengths, which is quite exceptional in these compounds. Two formulæ have been proposed for dehydracetic acid, one by Feist and the other by Collie:

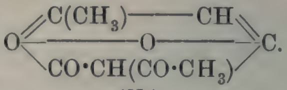

(Collie.)


(Feist.)

Whichever be the correct formula, it is evident that the ring must be bridged, for otherwise, the addition of alkali would increase the absorption considerably. Consequently the question of constitution lies between the two forms:

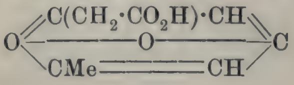

(I.)

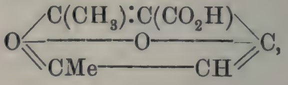
and


(II.)

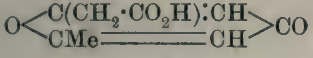
The very close similarity between triacetic lactone and dehydracetic acid in presence of alkali is necessarily strongly in favour of (I), since in (II) there is one more carbonyl group in direct conjugation than in triacetic lactone, which would presumably increase the play of forces and so alter the absorption. The increase of absorption in the free compound does not seem to follow, however, from either of the formulæ.

The absorption spectrum of dimethylpyronecarboxylic acid is shown in Fig. 4, curve 3, and presents some considerable interest. The formula of this compound from the method of preparation depends on that of dehydracetic acid. Two are possible, namely:


(I.)


(II.)

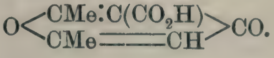
and, of these, (I) would follow if Collie's formula for dehydracetic acid were correct, and (II) if that of Feist were true. We have observed that the addition of sodium ethoxide to the alcoholic solution of this acid does not at once produce any very marked change in the absorption, but if this solution is kept standing for about a week, the type of absorption is quite altered and becomes like that of the open-chain form of diacetylacetone. It appears, therefore, that this acid, even in alcoholic solution in the presence of sodium ethoxide, is inclined to open up and favour the open-chain form. This tendency will naturally be antagonistic to the formation of the bridged ring, which is the final condensed form of the pyrones. Consequently in this compound we should expect to find some evidence that the whole does not exist in the bridged-ring form, and, indeed, the absorption curve shows a sudden extension or incipient absorption band in the same region of the spectrum as the band of the addition compound of dimethylpyrone and sodium ethoxide. Dimethylpyronecarboxylic acid, therefore, must exist in alcoholic solution to a great extent as



$$\mathrm{O}<\begin{matrix}\mathrm{C(CH_2\cdot CO_2H){:}CH}\\ \mathrm{CMe{=\!=\!=\!=}CH}\end{matrix}>\mathrm{CO}$$

(I.)

or



$$\mathrm{O}<\begin{matrix}\mathrm{CMe{:}C(CO_2H)}\\ \mathrm{CMe{=\!=\!=}CH}\end{matrix}>\mathrm{CO.}$$

(II.)

Since the region of the absorption is the same as that of the compound of dimethylpyrone and sodium ethoxide, formula (I) is the more probable, since (II) introduces a further conjugation of the carbonyl portion of the carboxyl group. This would mean, therefore, that Collie's formula is the more probable for dehydracetic acid, which agrees with the conclusion drawn above for this substance.

It is possible that the reason for this abnormal behaviour of dimethylpyronecarboxylic acid lies in the CH_2 group of the side-chain. It has been previously shown that in compounds of the type of benzyl methyl ether and benzyl alcohol, which contain in the side-chain a CH_2 group and some group possessing residual affinity, the absorption and dynamic activity of the benzene nucleus are much modified (Baly and Collie, Trans., 1905, **87**, 1332). The influence of a CH_2 group in this way is often very pronounced, although the reason for this is obscure (Baly and Tuck, Trans., 1908, **93**, 1902), and, further, it is not improbable that the increased absorption of dehydracetic acid (which is doubtless ketonic) in neutral solution is due to this cause.

Finally, we have observed the absorption spectrum of *iso*dehydracetic acid, which is shown in Fig. 4, curve 4, although the substance does not belong to the class of 4-pyrones.

A reference was made above to the much greater readiness with which sodium ethoxide forms the additive compound with pyrone than it does with dimethylpyrone. This fact was also noticed in the case of pyromeconic acid and triacetic lactone, for the addition takes place much more readily in the former case. In the case of pyrone one equivalent of sodium ethoxide is sufficient to form a considerable quantity of the additive compound, whereas upwards of eighty equivalents are required in the case of dimethylpyrone. Again, four equivalents are sufficient in the case of pyromeconic acid, and ten equivalents are entirely insufficient with triacetic lactone. There is therefore no doubt that the presence of the methyl groups on the neighbouring carbon atoms materially decreases the activity of the oxygen atom, this being comparable with the effect already examined in the ketones (Stewart and Baly, Trans., 1906, **89**, 507). This fact brings the observations within the class of phenomena usually known as steric hindrance.

Conclusions.

1. The results obtained indicate that pyrone, dimethylpyrone, and tetramethylpyrone exist in solution in the bridged-ring form.

2. Diacetylacetone in aqueous solution exists in the open-chain form and is an equilibrium mixture of the enolic and ketonic forms. In alcoholic solution this compound exists partly in the closed-ring form, that is to say, as a hydrate of dimethylpyrone.

3. Pyromeconic acid, triacetic lactone, diacetyldimethylpyrone, chelidonic acid, and its ethyl ester all possess the bridged-ring structure.

4. The bridge structure thus typical of the pyrones is broken in the presence of sodium ethoxide, due to the formation of an additive compound in each case, the addition of the sodium ethoxide being to the atom of oxygen in the ring.

5. Ethyl xanthochelidonate appears to exist in the open-chain form in dry ether or chloroform solution, which solutions are both colourless. In alcoholic or aqueous solution it exists as a mixture of the open-chain and closed-ring forms, and in alcoholic solution in presence of sodium ethoxide, entirely as the sodium salt of the closed-ring form.

6. The absorption spectrum of dehydracetic acid indicates that Collie's formula is more probable for this compound than that of Feist. This would lead to the conclusion that the so-called dimethylpyrone-β-carboxylic acid has not this formula, but the carboxyl group is attached to one of the methyl groups. This acid exhibits an absorption in agreement with this view, and, moreover, appears to exist partly with its ring unbridged.

In conclusion we have to express our thanks to Mr. Foster Spoxton and to Dr. H. Bassett for the valuable help they have given us in the investigation.

Spectroscopic Laboratory.
University College, London.

of

XXII.—*Action of Alcohols on Metallic Calcium.*

By FREDERICK MOLLWO PERKIN and LIONEL PRATT.

ABOUT twelve months ago (Proc., 1907, **23**, 304) we showed that calcium ethoxide is formed by the action of calcium on ethyl alcohol. The work has been extended, and it is now proposed to describe the compound in detail and its employment in organic synthesis. We have confined our work mainly, although not entirely, to calcium ethoxide, because this is the most easily produced alkyloxide and is of more general use.

When calcium is brought into contact with absolute alcohol, reaction may commence within the course of from thirty to sixty minutes, or no apparent action may ensue for three or four days, and then suddenly vigorous effervescence will commence, the reaction continuing until the whole of the calcium has been converted into the ethoxide. Probably this, at times, slow reaction is due to the metal being coated with a thin film of oxide; consequently reaction will not commence until the alcohol has made its way through this covering and has come into direct contact with the metal. When the mixture of alcohol and calcium is warmed on the water-bath, reaction will generally commence in a few minutes, and be complete within from one to two hours. We find it advantageous, in order that the reaction may be completed as rapidly as possible, to add from two to three times the theoretical amount of alcohol. The calcium ethoxide can be obtained free from alcohol by distilling the latter from an oil-bath at about 160°. This may either be done in an atmosphere of hydrogen or without taking this precaution. There is, of course, a slight tendency to oxidation on cooling when hydrogen is not employed, but this is very much less than in the corresponding preparation of dry sodium ethoxide. The small amount of alcohol vapour remaining in the apparatus probably prevents the oxidation, and when cold the calcium ethoxide is not deliquescent, and therefore does not oxidise so rapidly as the corresponding potassium or sodium compounds. As, however, it is necessary to allow it to cool in presence of alcohol vapour, the distilling flask must not be moved from the condenser until it is quite cold; otherwise if the hot product is exposed to the air, oxidation takes place and it becomes red-hot, smouldering away until it is completely decomposed. When cold, it is very readily detached from the distilling flask, because it contracts slightly on cooling, and usually gentle shaking is sufficient to break it up small enough to pour out of the neck of the flask.

Calcium ethoxide is a white substance with a slight tinge of yellow, but this yellow colour may very likely be due to traces of iron oxide, calcium carbide, and calcium oxide, which the metal contains. In fact, it is impossible to obtain calcium in the form of turnings without having the surface superficially oxidised, and traces of moisture in the alcohol would also tend to the formation of calcium oxide. The calcium turnings used by us were obtained from the Elektrochemische Fabrik, Bitterfeld.

The calcium ethoxide was analysed as follows: (*a*) A portion was ignited until constancy in weight was obtained. (*b*) The substance was dissolved in hydrochloric acid, neutralised with ammonia and precipitated as oxalate, and ignited as usual. (*c*) In another set of experiments it was converted into sulphate, but it was finally found that exactly the same results were obtained by employing the simpler method, namely, that of direct ignition. The substance evidently contained small quantities of calcium oxide, the best analysis obtained giving Ca = 34·7, whereas $Ca(OEt)_2$ requires Ca = 30·80 per cent.

We have also succeeded in obtaining calcium ethoxide in the form of crystals by boiling about 5 grams of metallic calcium with about 300 c.c. of absolute alcohol. A considerable portion of the ethoxide dissolves, and after allowing to settle and pouring off the supernatant liquid, the latter is slowly evaporated in an evacuated desiccator over calcium chloride. In the course of twenty-four hours or so, colourless crystals about 2 mm. in length separate out; as soon as they are removed from the alcohol, however, they commence to effloresce. The crystals appear to be octahedral, but owing to the efflorescence it was impossible exactly to determine their shape; sometimes, however, they separate in groups of needles. The moist substance was placed in an evacuated desiccator over sulphuric acid, and was analysed at the end of six (I), twenty-four (II), seventy-two (III), and ninety-six hours (IV), when it was found that the calcium content increased progressively, although after seventy-two hours the loss in alcohol which was taking place was very slow. It will thus be seen that the freshly-crystallised substance contains two molecules of alcohol of crystallisation, which is gradually lost, until finally the alcohol-free product is obtained.

I. Found, Ca = 18·26. $Ca(OEt)_2,2EtOH$ requires Ca = 18·04 per cent.
II. „ Ca = 19·80.
III. „ Ca = 23·80. $Ca(OEt)_2,EtOH$ „ Ca = 22·74 „
IV. „ Ca = 26·54. $Ca(OEt)_2$ „ Ca = 30·80 „

In another case some of the transparent crystals were placed in a desiccator containing calcium chloride, which had been used several times for drying other crystals and smelt strongly of alcohol. At the end of forty-eight hours they had not lost their transparency. On analysis:

Found, Ca = 18·25. $Ca(OEt)_2,2EtOH$ requires Ca = 18·04 per cent.

Analysis of Calcium Ethoxide dried at 170°.—About 10 grams of metallic calcium were boiled with a large excess of alcohol, and after all action had ceased the clear supernatant liquor was poured off from undissolved residue. This liquid was then placed in a distilling flask connected with a condenser and heated to 170° in an oil-bath, at the same time a rapid stream of dry hydrogen being passed over it. When all the alcohol had distilled off, the product was cooled, the current of hydrogen being meanwhile maintained. Analysis gave:

Found, Ca = 30·84. $Ca(OEt)_2$ requires Ca = 30·80 per cent.

It is thus evident that pure calcium ethoxide can be obtained by dissolving the impure product in ethyl alcohol and distilling off the excess of the solvent in a stream of hydrogen; but when it is allowed to crystallise out from the alcohol, it contains two molecules of alcohol of crystallisation.

Action of Calcium Hydride on Alcohols.—It seemed to be of interest to ascertain whether calcium hydride would react with alcohols in a similar manner to metallic calcium, and we find that when the hydride is left for a short time in contact with alcohols, reaction takes place and the calcium alkyloxide is produced. In fact, in cases where the alcohol only reacts slowly with metallic calcium, the action is much more rapid and vigorous when calcium hydride is employed. The final product, however, is not so pure as when metallic calcium is used, because the commercial calcium hydride does not generally contain more than 80 per cent. of the pure hydride, the impurities being calcium oxide and calcium nitride. In the case of ethyl alcohol, the pure substance can be produced by treating the product obtained from calcium hydride with excess of alcohol, separating it from undissolved material, and crystallising or distilling in a stream of hydrogen. With other alcohols, however, most of which exert very little solvent action on the alkyloxide, it is not possible to purify the product in this way.

Calcium ethoxide, when pure, is a white, amorphous powder, which reacts with water, yielding calcium hydroxide and alcohol. We have tried its action in place of sodium ethoxide in the following synthetical preparations.

Condensation of Ethyl Acetate.—Two hundred grams of ethyl acetate were heated with 20 grams of metallic calcium for twelve hours in a reflux apparatus. The product was worked up in the usual way for the preparation of ethyl acetoacetate, and 14 grams of the pure substance were obtained, which is a much poorer yield than is produced when metallic sodium is employed as condensing agent.

Condensation of n-*Propyl Iodide with Ethyl Acetoacetate.*—Five grams of metallic calcium were boiled with 25 c.c. of absolute alcohol in a reflux apparatus until action ceased, and the whole of the calcium was converted into ethoxide. The ethoxide was only partly dissolved, a considerable quantity remaining in suspension. Thirty-three grams of ethyl acetoacetate were then added, and the mixture was boiled for about five minutes, when 40 grams of *n*-propyl iodide were added. A clear solution resulted, and the mixture was boiled from six to eight hours. The clear, nearly neutral liquid was poured into water, slightly acidified with acetic acid, and worked up as usual. On fractionation, three fractions were obtained, namely, one at 100—130°, which consisted of unchanged propyl iodide; the second at 130—200°, which contained unchanged ethyl acetoacetate; and the third at 200—215°, which proved to be propyl acetoacetate. This, on refractionation, boiled constantly at 208°; the yield was 35 per cent. of the theoretical.

Condensation of Ethyl Iodide.—When ethyl iodide was condensed with ethyl acetoacetate by means of calcium ethoxide, a 56 per cent. yield of ethyl ethylacetoacetate was obtained.

Condensation of Diethylmalonate and Benzyl Chloride.—Twenty-two grams of metallic calcium were converted into ethoxide in 140 c.c. of absolute alcohol. When the action was complete, 160 grams of diethylmalonate (1 mol.) were added, when a vigorous action took place, the calcium ethoxide partly passing into solution. One hundred and twenty-six grams of benzyl chloride (1 mol.) were now added, and a clear, rather syrupy solution was obtained. The mixture was boiled under a reflux condenser for eight hours. The product, which had an acid reaction, was poured into a concentrated salt solution; this was extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried and evaporated, and the residue fractionated under 60 mm. pressure, when the following fractions were obtained:

160—190°, mainly ethyl malonate with a small quantity of benzyl chloride; 190—210°, mainly ethyl benzylmalonate (55 grams); 210—230°, mainly small intermediate fraction; 230—260°, mainly ethyl dibenzylmalonate (46 grams).

A portion of the fraction 230—260° was hydrolysed with alcoholic potash. On evaporating off the alcohol, dissolving in water, and acidifying with hydrochloric acid, dibenzylmalonic acid was obtained, which, on recrystallisation from glacial acetic acid, formed brilliant needle-shaped crystals, melting and evolving gas at 167°. A portion of the acid was heated in an oil-bath to 170—180° until all evolution of gas ceased. The residue crystallised from light petroleum in small, colourless needles, melting sharply at 92°. In the literature, the melting point of dibenzylacetic acid is given as 87°. In order to prove that the acid melting at 92° was dibenzylacetic acid, the silver salt was prepared and analysed:

Found, Ag = 31·10. $C_{16}H_{15}O_2Ag$ requires Ag = 31·11 per cent.

The fraction 190—210° was also hydrolysed, and the acid so obtained was crystallised from water, when it formed colourless needles, melting at 119°. The melting point of benzylmalonic acid is given in the literature as 117°. The silver salt was prepared and analysed, with the folowing result:

Found, Ag = 43·15. $C_{10}H_8O_4Ag_2$ requires Ag = 43·35 per cent.

The substance was therefore benzylmalonic acid. It was then heated on an oil-bath to 140° until carbon dioxide was no longer evolved, and the residue was crystallised from water. The melting point was found to be 47°, which proved it to be β-phenylpropionic acid.

These experiments show that when benzyl chloride and diethylmalonate are condensed by means of calcium ethoxide, the reaction proceeds in two directions, about equal quantities of ethyl benzylmalonate and ethyl dibenzylmalonate being produced, a small quantity of diethylmalonate and a trace of benzyl chloride remaining over. It seemed, therefore, of interest to effect the condensation, employing 2 mols. of benzyl chloride to 1 mol. of diethylmalonate.

Twelve grams of metallic calcium were converted into the ethoxide by heating with 100 grams of alcohol. Thirty-four grams of ethyl malonate and 53 grams of benzyl chloride were added, and the mixture was boiled under a reflux condenser for ten hours. At the end of the time, the slightly turbid liquid was worked up as previously described. On fractionation only about 5 grams of low boiling products were obtained, the bulk passing over at 226—228°/18 mm., and 53 grams, or 73·4 per cent. of the theoretical amount, being obtained. On hydrolysis, pure dibenzylmalonic acid was obtained.

Condensation of Benzyl Chloride with Methyl Cyanoacetate.—Thirteen grams of metallic calcium were converted into the ethoxide by using 70 c.c. of ethyl alcohol, and 50 grams of methyl cyanoacetate were added. A solid calcium salt separated out, which, on the addition of 64 grams of benzyl chloride, almost completely dissolved. The mixture was heated in a reflux apparatus for seven hours, and was then poured into water, acidified with acetic acid, and extracted with ether. From the ethereal solution a heavy oil was obtained, which on fractionation under a pressure of 15 mm. yielded three fractions, namely, (1) below 215°, mostly a mixture of benzyl chloride and unchanged methyl cyanoacetate, (2) 215—227°, and (3) 227—240°. On refractionation there was obtained, below 215°, 18·5 grams; at 215—230°, 14 grams; and at 235—240°, 33 grams. The highest boiling fraction, a portion of which was hydrolysed by alcoholic potash, was very viscid. The acid isolated on hydrolysis was crystallised from a mixture of toluene and light petroleum, when it melted at 145°. The silver salt of this was prepared and analysed:

Found, $Ag = 29{\cdot}30$. $C_{17}H_{15}O_2N$ requires $Ag = 29{\cdot}02$ per cent.

The acid is, therefore, dibenzylcyanoacetic acid. The fraction 215—230° was then hydrolysed with aqueous potassium hydroxide. The resulting acid was a viscid oil, which after a time slowly crystallised. An analysis of the silver salt showed it to be benzylcyanoacetic acid:

Found, $Ag = 38{\cdot}37$. $C_{10}H_9O_2N$ requires $Ag = 38{\cdot}28$ per cent.

The results obtained on condensing cyanoacetic esters with benzyl chloride are similar to those obtained when benzyl chloride is condensed with malonic ester, namely, the tendency is for two molecules of the benzyl group to pass into the cyanoacetic or malonic nucleus. This is probably due to the negative character of the benzyl radicle. As soon as one benzyl group has entered into the molecule, the negative character of the entire group is increased, and therefore reaction takes place with a further quantity of calcium ethoxide, with the result that a dibenzyl compound is produced. Consequently, small quantities of malonic or cyanoacetic ester and benzyl chloride remain when the reaction is over, but the malonic or cyanoacetic ester which is left over is greatly in excess of the benzyl chloride.

Other Alkyloxides.

Attempts were made to prepare alkyloxides from other alcohols, but in no case could such good results be obtained as with ethyl alcohol. The reactions commence much more slowly, and it is much more difficult to complete them. The reason appears to be due to the very slight solubility of the alkyloxides in the corresponding alcohols. Consequently the metal becomes coated with a protective covering of the alkyloxide, and further reaction proceeds exceedingly slowly. Alkyloxides have been prepared from methyl, *n*-propyl, butyl, and benzyl alcohols, but in no case could satisfactory analytical numbers be obtained. The analysis always showed an excess of from 5 to 10 per cent. of calcium, so that we have not proceeded further with the examination of these substances, particularly because the calcium ethoxide is so readily obtained, and, owing to its solubility in ethyl alcohol, is very suitable for various reactions. It should, however, be mentioned that the other alkyloxides are much more readily produced by using calcium hydride in place of metallic calcium; but as this substance is never pure, rarely containing more than 80 per cent. of the hydride, it follows that the alkyloxides thus prepared cannot be pure. There seems no reason, however, why they should not easily be prepared in the pure state were pure calcium hydride forthcoming.

Reduction of Nitrobenzene.—It was thought that perhaps calcium might be employed in place of sodium in the reduction of nitrobenzene and the formation of azoxybenzene. The nitrobenzene was dissolved in excess of methyl alcohol in the proportions required by the following equation:

$$4C_6H_5\cdot NO_2 + 3(CH_3O)_2Ca = 2C_{12}H_{10}ON_2 + 3(H\cdot CO_2)_2Ca + 6H_2O.$$

When metallic calcium is added directly to methyl alcohol the reaction is very slow, but when nitrobenzene is first added a vigorous reaction almost immediately takes place. The mixture as above was heated under a reflux condenser for about six hours, and the liquid filtered from the solid residue, which was washed with methyl alcohol. The filtrate was freed from alcohol by evaporation, and half of it was worked up in the usual way, the other half being distilled with iron filings to convert it into the azo-compound. Only small quantities, however, of azoxy- and azobenzene were obtained. That considerable reduction had taken place was proved by an examination of the solid residue, which contained a comparatively large amount of calcium formate. This method of preparation is, therefore, inferior to the older processes.

Experiments were also undertaken using ethyl alcohol in place of methyl alcohol, and in this case 21 per cent. of the theoretical quantity of azoxybenzene was obtained.

A portion of the expenses of this research have been met with a grant obtained from the Chemical Society, and the authors desire to express their thanks for the aid received.

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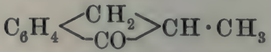
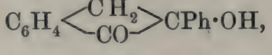
XXIII.—*The Atmospheric Oxidation of β-Methylhydrindone.*

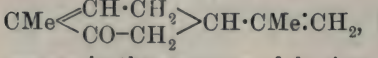
By Arthur H. Salway, Ph.D., B.Sc., and F. Stanley Kipping.

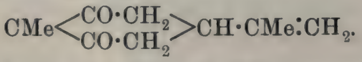
A small quantity of β-methylhydrindone,  $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>CH\cdot CH_3$ (Kipping and Clarke, Trans., 1903, **83**, 913), which had been freely exposed to the atmosphere for some time, was found to have deposited a considerable proportion of a crystalline solid. The object of the present investigation was to ascertain the nature of this transformation, and the results have shown that when this cyclic ketone is exposed to an atmosphere of oxygen, the latter is gradually absorbed with the formation of a mixture of oxidation products; from this mixture two acids, melting at 119—120° and 210° respectively, were isolated in small quantity, and these compounds were ultimately identified as benzylmethylketone-*o*-carboxylic acid and phthalic acid respectively. A small proportion of acetic acid and of a neutral compound melting at 211° were also separated; the amount of the latter substance was insufficient for further examination.

Several examples of the atmospheric oxidation of cyclic ketones are already on record. Miller (*Ber.*, 1892, **25**, 2095) has shown that β-phenylhydrindone, when shaken in ethereal solution with aqueous sodium carbonate, is oxidised to phenylbenzylketone-*o*-carboxylic acid, $C_6H_5\cdot CO\cdot CH_2\cdot C_6H_4\cdot CO_2H$, and β-hydroxy-β-phenylhydrindone,



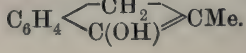
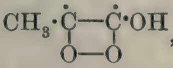
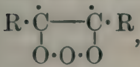
$$C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>CPh\cdot OH,$$

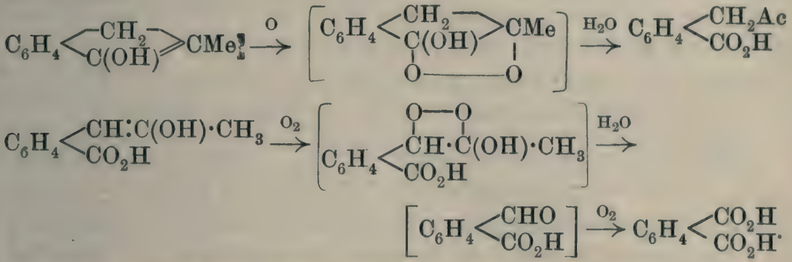
but the formation of phthalic acid was not observed. Harries, on the other hand (*Ber.*, 1901, **34**, 2105), has recorded the fact that carvone,  $CMe\lessgtr\genfrac{}{}{0pt}{}{CH\cdot CH_2}{CO-CH_2}>CH\cdot CMe{:}CH_2$, is slowly oxidised by atmospheric oxygen in the presence of barium hydroxide solution, with the formation of 1-methyl-4-propenyldihydroresorcinol,



$$CMe<\genfrac{}{}{0pt}{}{CO\cdot CH_2}{CO\cdot CH_2}>CH\cdot CMe{:}CH_2.$$

Our experiments seem to indicate that the presence of alkalis has no appreciable influence on the atmospheric oxidation of β-methylhydrindone.

In order to account for this unusual example of the disruption and subsequent degradation of a cyclic compound under the influence of atmospheric oxygen, it is necessary to assume that the ketone is first transformed into the enolic modification,  $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{C(OH)}\geqslant CMe$. It is then highly probable that the unsaturated grouping, $CH_3\cdot\dot{C}:\dot{C}\cdot OH$, forms an additive product,  $\begin{matrix}CH_3\cdot\dot{C}-\dot{C}\cdot OH\\ \;\;\;|\;\;\;\;\;\;|\\ \;\;\;O-O\end{matrix}$, with oxygen in much the same manner as unsaturated compounds, $R\cdot\dot{C}:\dot{C}R$, form ozonides,  $\begin{matrix}R\cdot\dot{C}-\dot{C}\cdot R\\ |\;\;\;\;\;\;|\\ O\cdot O\cdot O\end{matrix}$, with ozone; on treatment with water this additive product is decomposed with the formation of benzylmethylketone-*o*-carboxylic acid, the enolic modification of which undergoes a similar series of transformations with the ultimate formation of phthalic and acetic acids:



$$C_6H_4<\begin{matrix}CH_2\\C(OH)\end{matrix}>CMe \xrightarrow{O} \left[C_6H_4<\begin{matrix}CH_2\\C(OH)\\|\\O\end{matrix}\!\!-\!\!\!-\!\!>\begin{matrix}CMe\\|\\O\end{matrix}\right] \xrightarrow{H_2O} C_6H_4<\begin{matrix}CH_2Ac\\CO_2H\end{matrix}$$

$$C_6H_4<\begin{matrix}CH:C(OH)\cdot CH_3\\CO_2H\end{matrix} \xrightarrow{O_2} \left[C_6H_4<\begin{matrix}O-O\\|\;\;\;\;\;|\\CH\cdot C(OH)\cdot CH_3\\CO_2H\end{matrix}\right] \xrightarrow{H_2O}$$

$$\left[C_6H_4<\begin{matrix}CHO\\CO_2H\end{matrix}\right] \xrightarrow{O_2} C_6H_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}.$$

The fact that under ordinary conditions β-methylhydrindone seems to consist entirely of the ketonic form, which immediately passes into the enolic modification in presence of alkalis (Kipping, Proc., 1902, **18**, 34), does not invalidate this view of the mechanism of the oxidation process; the latter change takes place only very slowly, and even after several years' exposure to the atmosphere in an open beaker, a considerable proportion of the ketone is not yet oxidised.

The oxidation products, obtained by the action of potassium permanganate on β-methylhydrindone under varied conditions, were also examined. A considerable quantity of the ketone was always oxidised to phthalic acid, and variable amounts of *o*-carboxybenzoylformic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot CO_2H$, were obtained. In no case, however, was it possible to isolate the compound,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CO\cdot CH_3,$$

which is formed by the atmospheric oxidation of the ketone.

α-Hydrindone, like β-methylhydrindone, undergoes change on exposure to air, and is slowly converted into a brown oil, but we have not had an opportunity of investigating the nature of this product.

EXPERIMENTAL.

Atmospheric Oxidation of β-Methylhydrindone.

A number of experiments were carried out for the purpose of determining the most favourable conditions for the rapid oxidation of the ketone by air, but the results were inconclusive. The rate of oxidation was not appreciably increased by agitating ethereal solutions of the ketone with air in the presence of alkalis, and apparently the following method gave the best results. Thin layers of β-methylhydrindone were exposed for a long time to an atmosphere of moist oxygen, which was renewed at frequent intervals. After several months' exposure, the mixture of unchanged ketone and its oxidation products was digested with chloroform and the insoluble solid collected. This solid, which amounted to about 5 per cent. of the ketone employed in the oxidation, was acid in character, and melted, showing some decomposition, at 210°. It was purified by recrystallisation from water, and was thus obtained in clusters of colourless plates, which melted and decomposed at 212° when heated rapidly:

0·1336 gave 0·2834 CO_2 and 0·0473 H_2O. C = 57·9; H = 3·9.
$C_8H_6O_4$ requires C = 57·8; H = 3·6 per cent.

0·0934 required for neutralisation 11·1 c.c. *N*/10-NaOH. M.W. = 168.
A dibasic acid, $C_8H_6O_4$, requires M.W. = 166.

The analysis and titration indicated phthalic acid, and the identity of this oxidation product with that acid was confirmed by evaporating a portion of the product with acetic chloride, when it was converted into phthalic anhydride melting at 128°.

The chloroform solution, from which the phthalic acid had been removed as above described, was shaken with an aqueous solution of sodium carbonate until all acid had been removed. The alkaline extract was of a yellowish-red colour and, on acidification with dilute sulphuric acid, yielded an oil which rapidly became solid. This was completely extracted with ether, the ethereal solution washed with a little water, dried, and the ether removed, when a light brown, soft solid, amounting to about 20 per cent. of the ketone employed in the oxidation, was obtained. This product was crystallised several times from a mixture of benzene and light petroleum, from which it was deposited in radiating clusters of colourless needles melting at 119—120°:

0·1474 gave 0·3636 CO_2 and 0·0744 H_2O. C = 67·3; H = 5·6.
$C_{10}H_{10}O_3$ requires C = 67·4; H = 5·6 per cent.

0·1381 required for neutralisation 7·9 c.c. *N*/10-NaOH. M.W. = 175.
A monobasic acid, $C_{10}H_{10}O_3$, requires M.W. = 178.

The only possible monobasic acid of the empirical formula $C_{10}H_{10}O_3$, which could be produced by the oxidation of β-methylhydrindone, is benzylmethylketone-*o*-carboxylic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$. This compound has been already described by Gottlieb (*Ber.*, 1899, **32**, 965), who gives its melting point as 118°. The identity of the above compound with that of Gottlieb was completely established by the preparation of the oxime, which melted at 163°.

The mother liquors from the crystallisation of the above ketonic acid yielded on evaporation a brown oily substance, which showed no signs of crystallising. It was converted into the barium salt, and the latter fractionated, but we were unable to isolate any definite compound from it.

The chloroform solution containing the neutral products of oxidation was washed free from alkali, dried, and the chloroform evaporated. The residual oil was then distilled in a current of steam to remove unchanged methylhydrindone. There remained a small quantity of a semi-solid oil, amounting to about 3 per cent. of the ketone employed in the oxidation. It was extracted with ether, the ethereal solution dried, and the ether removed. The residue was dissolved in a little hot alcohol, and, after long standing, colourless needles melting at 211° were deposited. This substance was insoluble in water or light petroleum, but readily soluble in alcohol or benzene. It was not obtained in sufficient quantity for further examination. The mother liquors still contained a large proportion of this substance, and an attempt was made to isolate it from these in the form of an oxime, but without success.

The formation of acetic acid by the atmospheric oxidation of β-methylhydrindone was proved in a separate experiment. A quantity of the ketone was left for some time freely exposed to air in the presence of sodium carbonate, and ultimately acidified and distilled in a current of steam. The distillate was shaken once with ether to remove unchanged ketone, neutralised with barium hydroxide, and concentrated. The concentrated solution gave the reactions of an acetate.

Oxidation of β-Methylhydrindone with Potassium Permanganate.

Ten grams of β-methylhydrindone were shaken with water to form an emulsion, and a 2 per cent. solution of alkaline potassium permanganate (14 grams) added drop by drop with continual agitation at the ordinary temperature. When all had been added, the mixture was distilled in a current of steam to remove unchanged ketone, and then filtered. The alkaline filtrate was concentrated to a small bulk, acidified with dilute sulphuric acid, and extracted several times with ether. From the ethereal solution there was obtained a yellowish-brown oil, which soon became solid. It was digested with chloroform, and the insoluble portion collected. This amounted to 2 grams, and was identified as phthalic acid. The chloroform filtrate yielded on evaporation an oily acid which did not crystallise. It was purified by conversion into the barium salt, which separated from water in well-formed hexagonal plates :

0·2534, dried at 105°, gave 0·1790 $BaSO_4$. Ba = 41·5.
$C_9H_4O_5Ba$ requires Ba = 41·6 per cent.

The free acid corresponding with this barium salt was regenerated by the addition of dilute sulphuric acid and extracted with ether. The ethereal extract was washed with a few drops of water, dried, and the ether removed. An oily residue was obtained, which, after long standing, solidified to a hard, crystalline mass. It then melted at 143° :

0·1470 gave 0·2991 CO_2 and 0·0450 H_2O. C = 55·5 ; H = 3·4.
$C_9H_6O_5$ requires C = 55·7 ; H = 3·1 per cent.

The analysis and the properties of the above compound prove that it is identical with *o*-carboxybenzoylformic acid (compare Scherks, *Ber.*, 1885, **18**, 379, and Henriques, *Ber.*, 1888, **21**, 1609).

Other oxidation experiments, in which the amount of permanganate was varied from one atom of oxygen upwards per molecule of β-methylhydrindone, were carried out, but in all cases phthalic and *o*-carboxybenzoylformic acids were formed in variable amounts, and no other product of oxidation could be isolated.

If, on the other hand, hydrogen peroxide is employed as the oxidising agent, the reaction is apparently not more rapid than in the case of atmospheric oxidation.

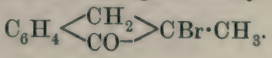
The Action of Bromine on β-Methylhydrindone.

Bromine water was caused to react with β-methylhydrindone with the object of ascertaining whether oxidation products other than phthalic acid could be obtained. On adding bromine water to an emulsion of the ketone with water and heating to 100° the bromine was readily absorbed, with the formation of an oily product, which rapidly solidified on cooling. This solid was collected and recrystallised from alcohol, from which it was deposited in large, flat prisms melting at 72—73° :

0·1771 gave 0·3485 CO_2 and 0·0661 H_2O. C = 53·7 ; H = 4·1.
0·3378 „ 0·2829 AgBr. Br = 35·6.
$C_{10}H_9OBr$ requires C = 53·3 ; H = 4·0 ; Br = 35·6 per cent.

These results indicate that the compound is a monobromo-substitution product of β-methylhydrindone.

Monobromo-β-methylhydrindone, $C_{10}H_9OBr$, crystallises from alcohol in colourless, well-formed prisms melting at 72—73°. It is readily soluble in the usual organic solvents, except light petroleum. It is best prepared by adding a slight excess of bromine to β-methylhydrindone in chloroform solution, and removing the excess of halogen by means of dilute sodium hydroxide. When it is oxidised with potassium permanganate in alkaline solution, phthalic acid is formed, which proves that the substitution has not taken place in the nucleus. Its constitution, therefore, is in all probability,



$$C_6H_4<{}^{CH_2}_{CO-}>CBr\cdot CH_3.$$

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XXIV.—*The Condensation of Oxymethylenecamphor with Primary and Secondary Amino-compounds.*

By WILLIAM JACKSON POPE and JOHN READ.

INFORMATION as to whether or not any particular primary or secondary amine is resolvable into enantiomorphously related isomerides may be obtained by the study of the acidic derivatives which it forms with an optically active acid chloride; if the amine is externally compensated it should yield two optically active and isomeric acidic derivatives, whilst if potentially inactive, or a pure optically active substance, it should form but one acidic derivative with the optically active acid chloride. A method of distinguishing between externally compensated and potentially inactive primary and secondary amino-compounds has been founded upon this argument by Kipping and Salway (Trans., 1904, **85**, 438); as the optically active acid chloride, these authors used *d*-benzylmethylacetyl chloride with very successful results. In view, however, of the difficulty of preparing the acid chloride in question and the readiness with which it undergoes optical inversion, it seems desirable that other more easily obtainable and more stable optically active substances capable of condensing with amines should be rendered available for the same purpose. With this amongst other objects, we have studied the condensation products of *d*-oxymethylenecamphor with primary and secondary bases for the purpose of ascertaining to what extent this substance can be used in the detection of external compensation in amines.

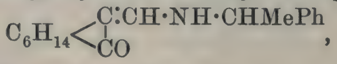
Oxymethylenecamphor is easily obtainable in quantity by the action of amyl formate and sodium on an ethereal solution of camphor as described by Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 331); we have found that it can be conveniently used for ascertaining whether a primary or secondary amine is or is not externally compensated.*

Condensation of d-*Oxymethylenecamphor with Externally Compensated α-Phenylethylamine.*

Externally compensated α-phenylethylamine, $NH_2\cdot CHMePh$, has been resolved by Lovén (*Ber.*, 1896, **29**, 2313; *J. pr. Chem.*, 1905, [ii], **72**, 307) and by Marckwald and Meth (*Ber.*, 1905, **38**, 801) into its optically active components; its resolution is not easy, and it yields partly racemic salts with *d*-camphorsulphonic acid (Pope and Harvey, Trans., 1899, **75**, 1110) and with *d*-bromocamphorsulphonic acid (Hunter and Kipping, Trans., 1903, **83**, 1149), so that these acids cannot be used to effect its resolution. It was therefore interesting to ascertain whether evidence of the externally compensated character of this base is obtainable by the use of *d*-oxymethylenecamphor.

Claisen and his co-workers have found (*loc. cit.*, p. 357) that condensation readily occurs on mixing a methyl-alcoholic solution of *d*-oxymethylenecamphor with a solution of a primary or secondary amino-compound in 30 per cent. acetic acid. On treating externally compensated α-phenylethylamine with the equivalent quantity of *d*-oxymethylenecamphor under these conditions, the interaction takes place at once, and an oil, which quickly solidifies, soon separates; the product is a mixture of two isomerides, and may be resolved by repeated crystallisation from hot alcohol. The less soluble isomeride, melting at 145—148°, is readily obtained in a state of purity, whilst the more soluble component, which melts at 112—114·5°, is purified by repeated crystallisation from dilute alcohol.

d-*α-Phenylethylamino*-d-*methylenecamphor*,



$$C_6H_{14}<\begin{matrix}C\colon CH\cdot NH\cdot CHMePh\\ |\\ CO\end{matrix},$$

This substance crystallises from alcohol in almost colourless, glistening prisms, which melt at 145—148°; the following results were obtained on analysis:

0·0922 gave 0·2724 CO_2 and 0·0781 H_2O. C = 80·58; H = 9·48.

$C_{19}H_{25}ON$ requires C = 80·50; H = 8·89 per cent.

On determining its specific rotatory power in various solvents, it was found that constant values are not immediately obtainable, because the compound exhibits mutarotation; although freshly prepared solutions are colourless, they develop a brown colour when preserved, and the rapidity with which the colour is produced appears to be paralleled by the velocity with which the specific rotatory power changes. The following determinations were made at the ordinary laboratory temperature in 2-dcm. tubes, the first reading in each series being taken as soon as possible after the substance had been dissolved.

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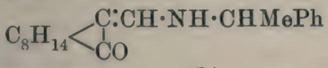
* As quantities of artificial and externally compensated camphor are now on the market, it is advisable to make sure, by determinations of rotatory power, that the material used in work such as that now described is pure *d*-camphor.

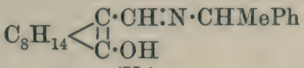
Solvent.	Weight in 20 c.c. (gram).	Time	α_D.	$[\alpha]_D$.
Benzene	0·1577	0	+5·67°	+359·5°
,, ...	0·1577	18 hours	+6·40	+405·9
,, ...	0·1577	18 days	−0·14	−8·9
,, ...	0·2050	0	+6·46	+315·1
,, ...	0·2050	18 hours	+8·45	+412·2
,, ...	0·2050	10 days	Solution too dark to read.	
Alcohol.........	0·0998	0	+2·55	+255·5
,, ...	0·0998	2 days	+3·05	+305·6
,, ...	0·0998	3 ,,	+3·15	+315·6
Acetic acid ...	0·1652	0	+5·03	+304·5
,, ...	0·1652	1 hour	+4·35	+263·3
,, ...	0·1652	2 days	+3·58	+210·7

The figures quoted above indicate that in benzene solution the rotatory power of *d*-*α*-phenylethylamino-*d*-methylenecamphor first increases and then decreases to a negative value with lapse of time; in alcoholic solution the rotatory power continually increases with time, but in glacial acetic acid solution the rotatory power progressively decreases during preservation of the solution. Premising that the changes of rotatory power are not caused by actual destruction of the compound, the results may be provisionally represented as due to the existence of dynamic isomerides, which possibly possess the following constitutions:



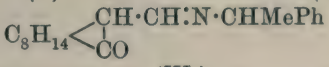
$$C_8H_{14}<\begin{matrix}C{:}CH\cdot NH\cdot CHMePh\\ |\\ CO\end{matrix}$$

(I.)



$$C_8H_{14}<\begin{matrix}C\cdot CH{:}N\cdot CHMePh\\ \|\\ C\cdot OH\end{matrix}$$

(II.)



$$C_8H_{14}<\begin{matrix}CH\cdot CH{:}N\cdot CHMePh\\ |\\ CO\end{matrix}$$

(III.)

Although in a preliminary survey of a new field, such as we now present, it is not possible to prove definitely the occurrence of dynamic isomerides of the actual constitutions above written, evidence can be adduced indicating that an explanation of this kind is necessary. The investigations of Claisen (*Annalen*, 1894, **281**, 306) show clearly that the simple derivatives of oxymethylenecamphor possess constitutions of the type of formula (I), and it is known (Armstrong and Lowry, *Proc. Roy. Soc.*, 1904, **72**, 258) that a trace of an alkaline catalyst hastens the establishment of isodynamic equilibrium in practically all the cases which have been studied. If, therefore, the substance of formula (II) or (III) is produced from that of formula (I) when the alcoholic solution is preserved, addition of a trace of sodium ethoxide to the alcoholic solution should accelerate the establishment of equilibrium between forms (I) and (II) or (III). The following determinations of the rotatory power of *d*-α-phenylethylamino-*d*-methylenecamphor in alcoholic solution to which a very small amount of sodium ethoxide had been added confirm this argument.

0·0982 gram, made up to 20 c.c. with ethyl alcohol containing a small quantity of sodium ethoxide, gave $\alpha_D + 3·15°$ in a 2-dcm. tube when examined as soon as possible after the preparation of the solution; whence $[\alpha]_D + 320·8°$. The rotatory power underwent no change during the subsequent lapse of three days. The addition of the small quantity of sodium ethoxide thus causes the specific rotatory power to assume in a few minutes approximately the maximum value which it attains after keeping the pure alcoholic solution for three days, namely, $[\alpha]_D + 315·6°$. This determination, whilst rendering highly probable the existence of an isomeride of the constitution (II) or (III), or perhaps both, also proves that the change of rotatory power is not due to destruction of the compound, because this result could not be brought about by the trace of catalyst used.

l-*α-Phenylethylamino*-d-*methylenecamphor.*

The more soluble substance produced during the condensation of *d*-oxymethylenecamphor with externally compensated α-phenylethylamine, after purification as described, melts at 112—114·5° and crystallises in almost colourless, soft needles. The following analytical results were obtained:

0·0882 gave 0·2597 CO_2 and 0·0740 H_2O. C = 80·30; H = 9·40.
$C_{19}H_{25}ON$ requires C = 80·50; H = 8·89 per cent.

As this substance has a lower dextrorotatory power than its isomeride, it is convenient to distinguish the two compounds by the prefixes *d*- and *l*-, applied as indicated above. The following determinations of the rotatory power of the lævo-isomeride were made in 2-dcm. tubes in the same solvents as in the previous case, and lead to the deduction of precisely similar conclusions.

It will be seen from these numbers that whilst a lapse of four days is necessary for *l*-α-phenylethylamino-*d*-methylenecamphor to acquire a constant specific rotation ($[\alpha]_D + 167·8°$) in pure alcoholic solution, an experimentally identical value ($[\alpha]_D + 168·1°$) is attained in one hour if a trace of sodium ethoxide is added to the alcoholic solution.

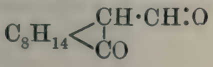
The fact that, quite apart from the isodynamic products, externally compensated α-phenylethylamine yields immediately two stereoiso-

Solvent.	Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
Benzene	0·1575	0	+2·98°	+189·2°
,,	0·1575	1·5 hours	+2·46	+156·2
,,	0·1575	3 ,,	+1·61	+102·2
,,	0·1575	4 ,,	+1·21	+76·8
,,	0·1575	18 days	−1·33	−84·4
Acetic acid	0·0857	0	+1·10	+128·4
,,	0·0857	24 hours	+1·10	+128·4
Alcohol	0·1043	0	+2·77	+265·6
,,	0·1043	1 day	+2·29	+219·6
,,	0·1043	2 days	+1·95	+187·0
,,	0·1043	3 ,,	+1·85	+177·4
,,	0·1043	4 ,,	+1·75	+167·8
Alcohol with trace of NaOEt	0·0922	0	+2·05	+222·3
,, ,, ,,	0·0922	1 hour	+1·55	+168·1
,, ,, ,,	0·0922	19 hours	+1·55	+168·1

meric condensation products with *d*-oxymethylenecamphor, shows that the latter substance can be used for the detection of external compensation in amino-compounds in much the same way as the *d*-benzylmethylacetyl chloride of Kipping and Salway. It does not appear, however, that a useful method of resolving such bases can be easily founded upon the use of oxymethylenecamphor, because the condensation products, as would be expected from their constitutions, strongly resist hydrolysis.

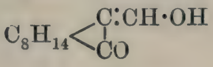
The Specific Rotatory Power of d-*Oxymethylenecamphor.*

Claisen pointed out (*loc. cit.*) that the following three constitutional formulæ were possible for oxymethylenecamphor:



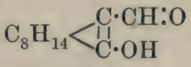
$$\mathrm{C_8H_{14}}<\begin{array}{l}\mathrm{CH{\cdot}CH{:}O}\\ \;|\\ \mathrm{CO}\end{array}$$

(I.)



$$\mathrm{C_8H_{14}}<\begin{array}{l}\mathrm{C{:}CH{\cdot}OH}\\ \;|\\ \mathrm{CO}\end{array}$$

(II.)



$$\mathrm{C_8H_{14}}<\begin{array}{l}\mathrm{C{\cdot}CH{:}O}\\ \;\|\\ \mathrm{C{\cdot}OH}\end{array}$$

(III.)

Brühl (*Zeitsch. physikal. Chem.*, 1900, **34**, 1) has made an extensive refractometric examination of oxymethylenecamphor in various solvents, and has decided that the substance exists only as an extremely stable enolic compound of the constitution (II); he concludes that no conversion into the form (I) takes place. Federlin (*Annalen*, 1907, **356**, 251) has contributed a series of colorimetric measurements of the substance in presence of ferric chloride, and similarly decides in favour of constitution (II). Neither of these two workers has discussed the possibility of the formation of equilibrium mixtures of the two enolic modifications (II) and (III), and it is, indeed, clear that neither the refractometric nor the colorimetric method lends itself to differentiating between these two forms. The following series of determinations of the rotatory power of *d*-oxymethylenecamphor shows this substance to exhibit marked mutarotation; the measurements were all made in 2-dcm. tubes.

A.—*Solutions in Ethyl Alcohol.*

Weight in 25 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1976	0	+3·19°	+201·8°
,,	4 hours	2·99	189·2
,,	7 ,,	2·99	189·2
,,	24 ,,	2·94	186·0
,,	72 ,,	2·94	186·0

The addition of a trace of sodium ethoxide caused no further change in the specific rotatory power.

B.—*Solution in Benzene.*

Weight in 25 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1563	0	+2·12°	+169·5°
,,	1 hour	1·79	143·2
,,	2 hours	1·63	130·4
,,	3·5 ,,	1·41	112·9
,,	5·5 ,,	1·24	99·2
,,	8·5 ,,	1·15	92·0
,,	36 ,,	1·10	88·0
,,	60 ,,	1·10	88·0
,,	20 days	1·01	80·8

Another preparation gave the following results:

C.—*Solution in Benzene.*

Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1652	0	+2·49°	+150·7°
,,	1 hour	1·35	81·7
,,	48 hours	1·28	77·5
,,	72 ,,	1·23	74·5

The following measurements were made with a sample of oxymethylenecamphor which, although originally of ordinary purity, had become yellow and sticky by lengthy preservation, as described by Claisen.

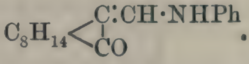
D.—*Solution in Benzene.*

Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1317	0	+1·67°	+126·8°
,,	1 hour	0·98	74·4
,,	24 hours	0·98	74·4

It is noteworthy that the mutarotation is much less marked in alcoholic than in benzene solution, and that the material which had undergone change as a result of preservation attains a constant rotatory power much more rapidly than does the freshly prepared substance. As the occurrence of the isodynamic change is in all probability conditioned by the presence of small quantities of impurity, and as these may change the equilibrium composition of the isodynamic mixture, it has not been thought advisable, at the present stage of the investigation, to attempt to apply the laws of mass action to the results obtained. Since *d*-oxymethylenecamphor exhibits mutarotation in alcohol and benzene solutions, and since the results of Brühl and of Federlin indicate that no considerable proportion of the material possesses the ketonic constitution (I), it seems justifiable to conclude that the two isodynamic forms of the enolic constitutions (II and III) are the main constituents. Oxymethylenecamphor appears to furnish the first observed instance of dynamic isomerism between two forms which contain active groups of the closely related constitutions shown in formulæ (II) and (III).

The mutarotation of the *a*-phenylethylamino-*d*-methylenecamphors cannot be seriously attributed to optical inversion of the secondary group in the basic component of the molecule; nevertheless, it seemed desirable to examine other compounds of the same type, prepared by using a potentially inactive base, in order to dispel any doubts that might remain as to the origin of the mutarotation. The following substances were therefore studied.

Anilino-d-*methylenecamphor*,

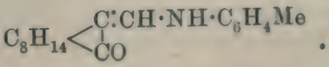


$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NHPh\\ \mid\\ CO\end{array}.$$

The aniline derivative of *d*-oxymethylenecamphor was obtained as an almost colourless, crystalline substance, melting at 167—170°, and agreeing in properties with the preparation of Bishop, Claisen, and Sinclair (*loc. cit.*, p. 357). The following determinations of its rotatory power were made in 2-dcm. tubes in benzene solution:

Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1524	0	+4·19°	+274·9°
,,	0·5 hour	4·10	268·4
0·3406	0	10·25	300·3
,,	4 hours	10·00	293·6
0·1018	0	3·15	309·4
,,	2 hours	2·78	273·1
,,	20 ,,	2·78	273·1

p-*Toluidino*-d-*methylenecamphor*,



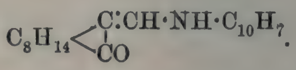
$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4Me\\ \mid\\ CO\end{array}.$$

The *p*-toluidine derivative was prepared by Claisen and his coworkers as a faintly yellow, crystalline substance melting at 188—189°. It is sparingly soluble in benzene, and on dissolving 0·15 gram in 20 c.c. of this solvent with the aid of heat and allowing to cool, the solution becomes filled with colourless, silky needles; after the lapse of half an hour, however, these re-dissolve, and the solution, which was originally colourless, acquires a reddish-brown tint. The following observations of the rotatory power were made:

0·0738 gram, made up to 20 c.c. with benzene, gave on immediate reading α_D +2·08° in a 2-dcm. tube; whence $[\alpha]_D$ +281·8°. After standing for ninety minutes, the value α_D +1·82° was obtained; whence $[\alpha]_D$ +246·5°. In benzene solution the substance therefore exhibits mutarotation.

0·1193 gram, made up to 20 c.c. with alcohol to which a trace of sodium ethoxide has been added, gave on immediate reading α_D +4·27° in a 2-dcm. tube; whence $[\alpha]_D$ +357·9°. This value remained unchanged during the subsequent two days; that no mutarotation is observed in the presence of the catalyst is to be attributed to the rapidity with which equilibrium is established.

β-Naphthylamino-d-*methylenecamphor*,



$$C_8H_{14}\Big<\begin{matrix}C{:}CH\cdot NH\cdot C_{10}H_7\\ |\\ CO\end{matrix}.$$

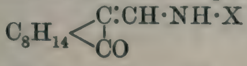
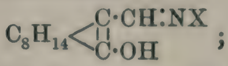
On mixing an alcoholic solution of *d*-oxymethylenecamphor with a solution of the corresponding quantity of β-naphthylamine in 30 per cent. acetic acid in the cold, reaction immediately sets in, and a copious, crystalline precipitate separates; when this is crystallised from hot alcohol, *β-naphthylamino*-d-*methylenecamphor* is obtained in yellow, crystalline scales melting at 184—187°:

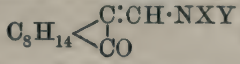
0·0986 gave 0·2978 CO_2 and 0·0684 H_2O. C = 82·37; H = 7·76.
$C_{21}H_{23}ON$ requires C = 82·56; H = 7·59 per cent.

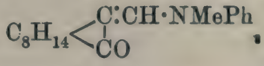
On dissolving 0·16 gram of the substance in 20 c.c. of benzene with the aid of heat and allowing to cool, the colourless solution deposits a white, crystalline material; this, however, rapidly re-dissolves, yielding a reddish-brown solution. The following determinations of rotatory power were made:

0·1085 gram, made up to 20 c.c. with benzene, gave α_D +2·87° in a 2-dcm. tube on immediate reading; whence $[\alpha]_D$ +264·6°. After standing for twenty-four hours, the value α_D +0·11° was obtained; whence $[\alpha]_D$ +10·1°. The substance thus exhibits the property of mutarotation in a very marked degree.

The above determinations of the rotatory powers of the condensation products of *d*-oxymethylenecamphor with the primary amino-compounds, aniline, *p*-toluidine, and β-naphthylamine, furnish conclusive evidence of the occurrence of isodynamic forms in the case of all these compounds. In accordance with the argument stated in connexion with the phenylethylamine derivatives, it is concluded that the two isodynamic forms concerned have, in the case of a given primary amino-compound, $NH_2{\cdot}X$, the constitutions


$C_8H_{14}\Big<\begin{array}{l}C{:}CH{\cdot}NH{\cdot}X\\ |\\ CO\end{array}$ and 
$C_8H_{14}\Big<\begin{array}{l}C{\cdot}CH{:}NX\\ ||\\ C{\cdot}OH\end{array}$;

the colour which is developed in solutions of the condensation products when kept may be attributed to the formation of the second form. It is to be noted, however, that whilst substances possessing constitutions of these two types may occur amongst the condensation products with primary amino-compounds, they cannot occur amongst the similar condensation products with secondary bases; for the latter constitutions of the type of 
$C_8H_{14}\Big<\begin{array}{l}C{:}CH{\cdot}NXY\\ |\\ CO\end{array}$ seem alone possible. If, therefore, our interpretation of the observations of mutarotation recorded in the previous pages is correct, it is to be anticipated that when *d*-oxymethylenecamphor is condensed with secondary amines, the products will not exhibit mutarotation; the behaviour of the following substance fully substantiates this prediction.

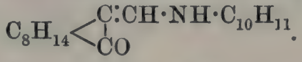
Methylanilino-d-*methylenecamphor*, 
$C_8H_{14}\Big<\begin{array}{l}C{:}CH{\cdot}NMePh\\ |\\ CO\end{array}$.

This substance, which was prepared by Claisen (*loc. cit.*, p. 360), is best obtained with the aid of 50 per cent. acetic acid; when recrystallised it is quite colourless, and melts sharply at 124°. The following determinations of its rotatory power were made in 2-dcm. tubes:

Solvent.	Weight in 20 c.c. (gram).	a_D.	$[a]_D$.
Benzene	0·1238	+5·10°	+412·0°
,,	0·1273	5·25	412·4
Alcohol with trace of NaOEt	0·1029	4·25	413·0

In each case the rotatory power was determined as quickly as possible after the solution had been made up, and the initial readings agree with readings taken at intervals during several days. It is also to be observed that the solutions differ in behaviour from those of the condensation products with primary bases, in that they remain perfectly colourless; further, the methylaniline condensation product was easily obtained colourless by crystallisation, whilst the colour of the products with aniline, *p*-toluidine, and *β*-naphthylamine could only be reduced to a yellow tint by prolonged fractional crystallisation. It is thus quite clear that the behaviour of methylanilinomethylenecamphor affords strong confirmation of the explanation advanced above of the mutarotation observed in the previous cases.

ac-*Tetrahydro-β-naphthylamino*-d-*methylenecamphor*,



$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_{10}H_{11}\\ \vert\\ CO\end{array}.$$

For reasons which are developed below, it appeared important to examine the condensation product of externally compensated *ac*-tetrahydro-β-naphthylamine with *d*-oxymethylenecamphor. This substance was prepared by the method previously used, and was easily purified by crystallisation from hot alcohol. A careful fractional crystallisation of the whole product showed it to be a single substance, which crystallises from alcohol in glistening, nearly colourless plates melting at 141—144°:

0·0878 gave 0·2625 CO_2 and 0·0708 H_2O. C = 81·54 ; H = 9·02.

$C_{21}H_{27}ON$ requires C = 81·49 ; H = 8·80 per cent.

On fractionally recrystallising the first and the last fractions of the product from hot alcohol, and determining the rotatory powers of the first fraction from the former and the last fraction from the latter, the following results were obtained.

First fraction from Benzene.

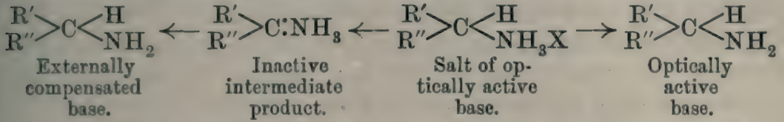
Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·0821	0	+1·66°	+202·2°
,,	18 hours	1·09	132·7
,,	24 ,,	1·03	125·4

Last fraction from Benzene.

Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·1002	0	+2·03°	+202·6°
,,	18 hours	1·40	139·7
,,	24 ,,	1·30	129·7

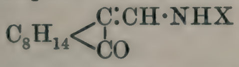
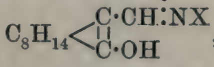
No further change in rotatory power occurred on longer standing, and it is obvious from the almost identical results obtained that the two samples, representing the first and the last separations, consist of the same substance; that the compound is not merely β-naphthylamino-*d*-methylenecamphor is at once evident from a comparison of the specific rotatory powers. In order to derive indications for further work on this case, it is desirable to form some provisional conception as to why *d*-oxymethylenecamphor only yields one condensation product with the externally compensated *ac*-tetrahydro-β-naphthylamine, whilst with externally compensated α-phenylethylamine it behaves normally and gives the two stereoisomeric products described above.

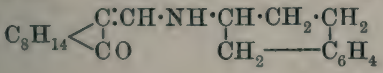
It has been shown (Pope and Harvey, Trans., 1901, **79**, 71) that externally compensated *ac*-tetrahydro-β-naphthylamine can be resolved into its enantiomorphously related components by crystallisation with *d*- or *l*-bromocamphorsulphonic acid, but that on liberating the base from the two salts *d*B*d*A and *l*B*l*A, which are easily obtained pure, optical inversion occurs to such an extent that the liberated bases exhibit but slight optical activity. The comparison of this case with the results obtained by Fischer with leucine (*Ber.*, 1900, **33**, 2370) and glutaminic acid (*Ber.*, 1899, **32**, 2466), and by Armstrong with phenylacetylchloroamine (Trans., 1900, **77**, 1049), led to the optical inversion which attends the action of alkali on the salts of the pure optically active tetrahydronaphthylamines being explained by the liberation of the base occurring in the following two kinds of ways when the components, HX, of the acid are removed from the salts.



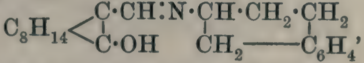
$$\begin{array}{c}R'\\R''\end{array}\!\!>C<\!\!\begin{array}{c}H\\NH_2\end{array} \leftarrow \begin{array}{c}R'\\R''\end{array}\!\!>C{:}NH_3 \leftarrow \begin{array}{c}R'\\R''\end{array}\!\!>C<\!\!\begin{array}{c}H\\NH_3X\end{array} \rightarrow \begin{array}{c}R'\\R''\end{array}\!\!>C<\!\!\begin{array}{c}H\\NH_2\end{array}$$

Externally compensated base.
Inactive intermediate product.
Salt of optically active base.
Optically active base.

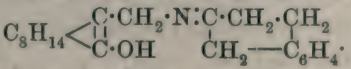
If the partial optical inversion which attends the liberation of *d*- or *l*-tetrahydro-*β*-naphthylamine from its pure salts be due to the removal of the components, HX, of the acid occurring in the two kinds of ways above represented, it is to be concluded that *ac*-tetrahydro-*β*-naphthylamine is distinguished from most primary bases by a tendency of the carbon atom attached to the amino-group to become doubly bound to the nitrogen atom. It has been sufficiently indicated above that the isomerism exhibited by the basic derivatives of oxymethylenecamphor necessitates the existence of isodynamic forms of the types:  $C_8H_{14}<\!\!\begin{array}{l}C{:}CH{\cdot}NHX\\CO\end{array}$ and  $C_8H_{14}<\!\!\begin{array}{l}C{\cdot}CH{:}NX\\C{\cdot}OH\end{array}$, the latter of which contains a doubly bound nitrogen atom in the molecule; these formulæ become, for the tetrahydronaphthylamine derivatives:

(*a*) 

$$C_8H_{14}<\!\!\begin{array}{l}C{:}CH{\cdot}NH{\cdot}CH{\cdot}CH_2{\cdot}CH_2\\CO\qquad\quad CH_2\text{——}C_6H_4\end{array}$$

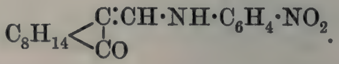
and (*b*) 

$$C_8H_{14}<\!\!\begin{array}{l}C{\cdot}CH{:}N{\cdot}CH{\cdot}CH_2{\cdot}CH_2\\C{\cdot}OH\quad CH_2\text{——}C_6H_4\end{array},$$

in both of which the original asymmetric carbon atom of the basic part is still present. The view already adopted, that the optical inversion attending the liberation of the tetrahydronaphthylamines from their salts is due to a tendency of the nitrogen atom to become doubly linked to the asymmetric carbon atom, leads, however, to the suggestion that the double linking between carbon and nitrogen in the enolic form (*b*) of the oxymethylene derivative could tend to become produced in the same position a in the base itself; under these conditions, the enolic isomeride of the substance (*a*) would be, not (*b*), but (*c*), namely,  $C_8H_{14}<\!\!\begin{array}{l}C{\cdot}CH_2{\cdot}N{:}C{\cdot}CH_2{\cdot}CH_2\\C{\cdot}OH\quad CH_2\text{—}C_6H_4\end{array}$. If the forms (*a*) and (*c*) are assumed by the dynamic isomerides, the substance should behave as does *ac*-tetrahydro-*β*-naphthylamino-*d*-methylenecamphor, and afford on examination no evidence that the basic part of the molecule contains an asymmetric carbon atom.

Since it has been shown above that the addition of an alkaline catalyst, namely, sodium ethoxide, greatly accelerates the isomeric change of the substances described, and presumably therefore hastens the production of the second form from the first, it might be anticipated that the introduction of strongly acidic groups into the molecule would lead to the suppression, either partly or completely, of one form; under these conditions, the dynamic isomerism, and consequently also the property of mutarotation, would not be observed. The requisite acidic groups can be conveniently introduced by substituting the primary base, aniline, for instance, by its nitro-derivatives; we have therefore examined the condensation products of *d*-oxymethylenecamphor with the three nitroanilines.

o-*Nitroanilino*-d-*methylenecamphor*, $C_8H_{14}<$



$$C_8H_{14}\Big\langle\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4\cdot NO_2\\ \;| \\ CO\end{array}.$$

o-Nitroaniline and *d*-oxymethylenecamphor interact readily under the conditions already described, and the product may be purified by recrystallisation from hot alcohol, in which it is sparingly soluble. It is ultimately obtained in long, dark red needles melting at 157—158°:

0·0987 gave 0·2447 CO_2 and 0·0616 H_2O. C = 67·62; H = 6·98.
$C_{17}H_{20}O_3N_2$ requires C = 67·94; H = 6·71 per cent.

0·0840 gram, made up to 20 c.c. with benzene, gave on immediate examination α_D + 2·42° in a 2-dcm. tube; whence $[\alpha]_D$ + 288·1°. No change in rotatory power was observed during the week following the preparation of the solution.

p-*Nitroanilino*-d-*methylenecamphor*.

This substance was prepared in the usual way; it crystallises from hot alcohol in long, orange-yellow needles melting at 154—155°:

0·1040 gave 0·2582 CO_2 and 0·0668 H_2O. C = 67·71; H = 7·10.
$C_{17}H_{20}O_3N_2$ requires C = 67·94; H = 6·71 per cent.

0·0804 gram, made up to 20 c.c. with benzene, gave on immediate examination α_D + 2·87° in a 2-dcm. tube; whence $[\alpha]_D$ + 356·9°. No change in rotatory power was observed during the week following the preparation of the solution.

m-*Nitroanilino*-d-*methylenecamphor*.

This substance is readily prepared in the customary manner, and on recrystallisation from hot alcohol, in which it dissolves readily, is obtained in small, yellow crystals melting at 167—168°:

0·1006 gave 0·2519 CO_2 and 0·0624 H_2O. C = 68·29; H = 6·94.
$C_{17}H_{20}O_3N_2$ requires C = 67·94; H = 6·71 per cent.

The following determinations of the rotatory power were made in benzene solution in 2-dcm. tubes:

Weight in 20 c.c. (gram).	Time.	α_D.	$[\alpha]_D$.
0·0821	0	+2·21°	+269·2°
,,	24 hours	1·92	233·9
,,	7 days	1·82	221·7

In view of possible interaction between these nitro-derivatives and sodium ethoxide, it was not anticipated that useful results would ensue immediately from examining the action of the alkaline catalyst on the three substances just described.

The above results show that the *o*- and *p*-nitroanilino-*d*-methylenecamphors exhibit no mutarotation; this is entirely in accordance with the anticipation expressed above. The *m*-nitroaniline derivative, however, differs markedly from its isomerides, in that it still exhibits the property of mutarotation, although the establishment of equilibrium is a very slow process in this case. The difference in behaviour between the *o*- and *p*-compounds, on the one hand, and the *m*-derivative, on the other, is in accordance with the view that in configuration, *o*- and *p*-isomerides are in mutual close relationship and entirely lacking in similarity with the corresponding *m*-derivatives (compare Barlow and Pope, Trans., 1906, **89**, 1697).

The investigation described in the present paper confirms the view, which has already been acted upon with success by Armstrong and his pupils, that more direct information concerning dynamic isomerism may, in appropriately selected cases, be derived by the study of optical activity than of chemical behaviour.

The further examination of the class of substances dealt with above is in progress.

THE CHEMICAL LABORATORIES,
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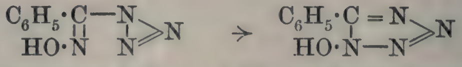
XXV.—*The Triazo-group. Part VII. Interaction of Benzhydroximic Chloride and Sodium Azide.*

By Martin Onslow Forster.

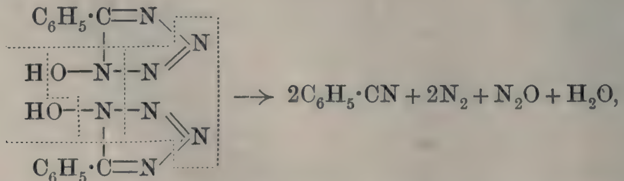
Bearing in mind the tendency displayed by the nitrogen atoms of the triazo-complex to undergo rearrangement, it seemed possible that benzhydroximic azide might be transformed into the isomeric tetrazole derivative by the influence of light or of some catalytic agent:



Benzhydroximic Azide 1-Hydroxy-5-phenyltetrazole

On attempting to prepare the first-named compound by the interaction of benzhydroximic chloride and sodium azide, however, the product was found to have properties indicating the tetrazole derivative rather than the substituted azoimide, and it must be concluded that the ethenoid linking of the benzhydroximic nucleus is endowed with sufficient residual affinity to effect the redistribution represented above independently of external chemical agency.

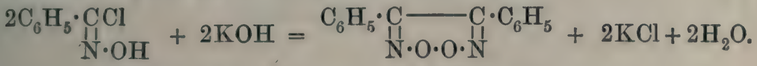
The problem of deciding the claims of the above formulæ to represent the product of interaction between benzhydroximic chloride and sodium azide is not difficult, although the behaviour of the substance towards sulphuric acid, stannous chloride, or sodium hydroxide might be construed in favour of either representation. The action of concentrated sulphuric acid leads to mild detonation and charring, whilst the diluted agent liberates one-half the nitrogen, a result which might be expected from benzhydroximic azide; the same proportion of gas is evolved when the substance is treated with stannous chloride in hydrochloric acid, whilst hot alkali hydroxide yields a quantity somewhat in excess of one-half the total nitrogen, a result most likely due to the production of nitrous oxide. Such behaviour, accompanied as it is by the formation of benzonitrile, clearly supports the tetrazole structure,



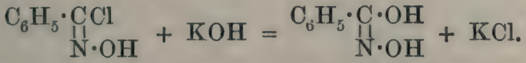
$$\longrightarrow 2C_6H_5\cdot CN + 2N_2 + N_2O + H_2O,$$

although it might be urged, on the other hand, that the decomposition was preceded by transformation of the azoimide into the tetrazole.

The most convincing exclusion of the triazo-group, however, is furnished by comparison of the material with benzhydroximic chloride itself (Werner and Buss, *Ber.*, 1894, **27**, 2193). A solution of the latter substance in alcohol becomes turbid immediately when treated with silver nitrate, the turbidity rapidly intensifying to a precipitate of silver chloride when the liquid is warmed; benzhydroximic azide would be expected to yield silver azide in similar circumstances, and the non-formation of this compound seems crucial. Moreover, when alkali hydroxide acts on benzhydroximic chloride, two courses, both distinct from the one already indicated in connexion with the substance under discussion, are followed, each one depending on elimination of hydrogen chloride, which is accompanied either by benzildioxime peroxide, or by benzhydroxamic acid:

I. 

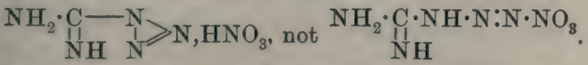
$$2C_6H_5\cdot\underset{\underset{N\cdot OH}{\|}}{C}Cl + 2KOH = C_6H_5\cdot\underset{\underset{N\cdot O\cdot O\cdot N}{\|\qquad\qquad\|}}{C\text{———}C}\cdot C_6H_5 + 2KCl + 2H_2O.$$

II. 

$$C_6H_5\cdot\underset{\underset{N\cdot OH}{\|}}{C}Cl + KOH = C_6H_5\cdot\underset{\underset{N\cdot OH}{\|}}{C}\cdot OH + KCl.$$

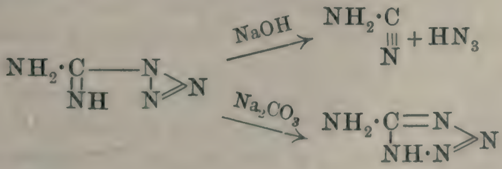
The absence of alkali azide from the products of decomposing the supposed hydroxyphenyltetrazole with potassium hydroxide is, therefore, highly significant. Furthermore, in presence of dilute alkali, it is possible to obtain well-defined benzoyl, *p*-toluenesulphonyl, and β-naphthalenesulphonyl derivatives, which could not be expected from benzhydroximic azide.

The transformation of benzhydroximic chloride into hydroxyphenyltetrazole recalls the experiments of Thiele (*Annalen*, 1892, **270**, 1) with "diazoguanidine." This compound, obtained as a nitrate on adding sodium nitrite to a solution of aminoguanidine nitrate in nitric acid, was recognised subsequently by Hantzsch and Vagt (*Annalen*, 1901, **314**, 339) as carbaminoiminoazoimide,



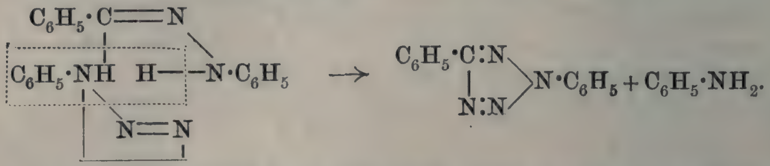
$$NH_2\cdot\begin{array}{c}C\text{—}N\\ \|\qquad|\\ NH\quad N\end{array}\!\!>N,HNO_3, \text{ not } NH_2\cdot\underset{\underset{NH}{\|}}{C}\cdot NH\cdot N{:}N\cdot NO_3.$$

Thiele found that although alkali hydroxides resolve carbaminoiminoazoimide into cyanamide and hydrazoic acid, alkali carbonates effect a simple rearrangement of the atoms into aminotetrazole, a transformation realised also by dilute acids, although accompanied in this case by elimination of hydrazoic acid:



Comparing the relative position of the triazo-group and azethenoid linking with the situation of the amino-radicle in carbaminoimino-azoimide on the one hand, and with that of the phenyl complex in benzhydroximic azide on the other, it will be recognised that exact analogy prevails, whence the production of hydroxyphenyltetrazole is readily understood.

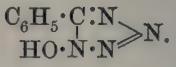
A somewhat similar, although not strictly analogous, instance of tetrazole formation was brought to light quite recently by Dimroth and Merzbacher (*Ber.*, 1907, **40**, 2402), who found that under the influence of sodium ethoxide, 1 : 3-diphenyltetrazole arises from phenylazoimide and benzylidenephenylhydrazone, with removal of aniline:



In this case, however, the triazo-group loses one atom of nitrogen, whereas the tetrazole-formation occurring when benzhydroximic chloride acts on sodium azide is the outcome of affinity rearrangement unaccompanied by loss of material.

Experimental.

1-*Hydroxy-5-phenyltetrazole*,



$$\begin{matrix}C_6H_5\cdot C:N \\ | \\ HO\cdot N\cdot N\end{matrix}\!\!>\!N.$$

Benzhydroximic chloride was prepared according to the directions of Werner and Buss (*Ber.*, 1894, **27**, 2197), and melted at 52° after being twice recrystallised from light petroleum. Either the substance itself, or some impurity retained tenaciously by it, has an intensely disagreeable effect on the skin, which becomes attacked by an irritating rash; this outbreak not only persists during several days, but is liable to affect parts of the body not brought into direct contact with the material.

In order to convert the chloro-compound into the tetrazole, a 10 per cent. ethereal solution containing slight excess of the calculated amount of powdered sodium azide in suspension was allowed to remain at the laboratory temperature during two or three days, a few grams of dehydrated sodium sulphate having been previously added for the purpose of checking, by exclusion of moisture, any tendency towards elimination of hydrogen chloride and consequent liberation of hydrazoic acid. The filtered solution having been quickly evaporated by a current of dry air, the colourless residue was recrystallised without delay from hot petroleum (b. p. 60—80°), of which about 200 c.c. are required by one gram; as the product is liable to undergo decomposition if left in the mother-liquor longer than one hour, it was precipitated by cooling, when the lustrous, transparent, snow-white needles were found to melt at about 124°, with vigorous intumescence :

0·0837 gave 25·2 c.c. N_2 at 18° and 764 mm. N = 34·96.
$C_7H_6ON_4$ requires N = 34·57 per cent.

Although more than 50 grams of the substance have been obtained in this manner, it is not advisable to transform a greater quantity than 5 or 10 grams of the benzhydroximic chloride at one operation, because the tetrazole is a short-lived compound, and even when purified undergoes spontaneous decomposition within three days, leaving a residue of benzonitrile, and liberating gas which contains a certain proportion of nitric oxide ; this alteration takes place irrespective of environment, specimens behaving in the same way whether exposed to, or protected from, light, either in air, an acid-desiccator, an alkali-desiccator, or in one containing both acid and alkali.

Hydroxyphenyltetrazole is freely soluble in cold acetone, ethyl acetate, or ethyl alcohol, crystallising from the last-named in lustrous, transparent prisms on dilution with water ; it is readily soluble in hot chloroform, from which it crystallises in needles on immediate cooling, but if the mother-liquor remains warm during a few minutes succeeding filtration, it becomes pale brown, and deposits benzonitrile alone on evaporation. The alcoholic solution does not precipitate sodium azide when treated with silver nitrate even on boiling, but it reduces an ammoniacal solution of silver oxide. Unlike benzhydroxamic acid, the tetrazole does not develop colour with ferric chloride.

Spontaneous Decomposition.—Seventeen grams of hydroxyphenyltetrazole which had not been recrystallised were allowed to undergo spontaneous decomposition, taking the form of vigorous intumescence accompanied by liquefaction; the escaping gas appeared to be nitrogen mixed with nitric oxide, and in view of the behaviour of the substance towards alkali it is probable that nitrous oxide also was present. Hydrazoic acid, hydrazine, hydroxylamine, and ammonia were not produced. The pale yellow liquid residue weighed 11 grams, consisting of benzonitrile and water; the nitrile boiled steadily at 188° under 760 mm. pressure, and as the result of a test with phenylhydrazine was evidently free from benzaldehyde. Hydroxyphenyltetrazole does not explode when heated, but the rush of gas at the melting point is very violent.

Action of Alkalis.—Hydroxyphenyltetrazole is insoluble in ammonia and in sodium carbonate, but alkali hydroxides dissolve it readily, and when the solution is gently warmed, vigorous effervescence takes place, followed by separation of benzonitrile. On decomposing one gram of the substance and removing the nitrile with ether, the alkaline liquid was indifferent towards Fehling's solution even when boiled, and did not give evidence of the presence of alkali nitrite or azide. The presence of nitrous oxide in the escaping gas was suspected, however, because quantitative examination gave on each occasion a result in excess of that which would be expected if one-half the nitrogen content appeared in elemental form:

0·1934 gave 34·7 c.c. N_2 at 18° and 761 mm. N = 20·75.
$C_7H_6ON_4$ requires $\frac{1}{2}$N = 17·26 per cent.

The experiments, of which the foregoing is an example, were conducted with 50 per cent. potassium hydroxide, but with a concentration of 10 per cent. it is easy to recognise the formation of a crystalline potassium derivative, which undergoes decomposition with rise of temperature.

Decomposition with Stannous Chloride.—The behaviour of the tetrazole derivative towards stannous chloride in hydrochloric acid is that which would have been anticipated from benzhydroximic azide:

0·2017 gave 29·1 c.c. N_2 at 17° and 761 mm. N = 16·76.
$C_7H_6ON_4$ requires $\frac{1}{2}$N = 17·26 per cent.

The liberation of gas is regular, and benzonitrile does not appear.

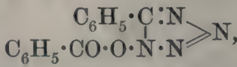
Action of Sulphuric Acid.—The tetrazole does not dissolve in cold, dilute sulphuric acid, but, when added to the concentrated agent, is immediately decomposed, evolving gas with mild detonation and charring, unless the substance is introduced, a few crystals at a time, into the vigorously shaken acid; nitric oxide and hydrazoic acid could not be detected, and the only recognised product besides nitrogen was benzoic acid, which separated in crystals on diluting the liquid. Owing to the violence of the action it was necessary to dilute the acid with half its volume of water for the purpose of gasometric experiments, and with this concentration the removal of nitrogen was not completed even on raising the temperature:

0·2070 gave 29·7 c.c. N_2 at 18° and 760 mm. N = 16·57.
$C_7H_6ON_4$ requires $\frac{1}{2}$N = 17·26 per cent.

The liquid, when rendered alkaline, did not reduce Fehling's solution.

Derivatives of Hydroxyphenyltetrazole.

The *benzoyl* derivative,



$$\begin{array}{r} C_6H_5\cdot C{:}N \\ | \quad \\ C_6H_5\cdot CO\cdot O\cdot N\cdot N \end{array}\!\!>\!N,$$

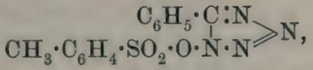
was obtained from benzoyl chloride and an alkaline solution of the potassium derivative; it is moderately soluble in boiling alcohol, from which it crystallises in lustrous, snow-white needles:

0·1500 gave 27·4 c.c. N_2 at 16° and 763 mm. N = 21·38.

$C_{14}H_{10}O_2N_4$ requires N = 21·05 per cent.

The substance dissolves very sparingly in boiling petroleum, from which it separates in stellate aggregates; the melting point is 127°, when decomposition takes place.

The p-*toluenesulphonyl* derivative,



$$\begin{array}{l}\quad\quad\quad\quad\quad C_6H_5\cdot C{:}N \\ CH_3\cdot C_6H_4\cdot SO_2\cdot O\cdot N\cdot N\end{array}\!\!\geqslant N,$$

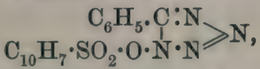
prepared by shaking 1 gram of the tetrazole dissolved in 5 per cent. potassium hydroxide with 3 grams of *p*-toluenesulphonyl chloride in 10 c.c. of ether, until the aqueous liquid no longer yielded benzonitrile and nitrogen when boiled, crystallised from light petroleum in transparent, rhomboidal prisms:

0·1108 gave 16·8 c.c. N_2 at 14° and 767 mm. N = 18·01.

$C_{14}H_{12}O_3N_4S$ requires N = 17·72 per cent.

The substance melts and evolves gas at 91—92°, and is scarcely soluble in cold petroleum. The first attempt to prepare it was made in presence of sodium carbonate instead of potassium hydroxide, and the only product was benzonitrile.

In the case of the *β-naphthalenesulphonyl* derivative,



$$\begin{array}{l}\quad\quad\quad C_6H_5\cdot C{:}N \\ C_{10}H_7\cdot SO_2\cdot O\cdot N\cdot N\end{array}\!\!\geqslant N,$$

also, interaction between the sulphonyl chloride and the tetrazole was too sluggish in presence of sodium carbonate, and benzonitrile was formed; in presence of alkali hydroxide, however, union was complete in a few minutes, and the product was obtained on evaporating the ether:

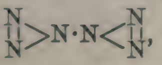
0·1507 gave 21·3 c.c. N_2 at 21° and 768 mm. N = 16·27.

$C_{17}H_{12}O_3N_4S$ requires N = 15·91 per cent.

The substance dissolves readily in hot, absolute alcohol, crystallising in lustrous needles, which melt and decompose at 101°.

Unsuccessful Attempt to Prepare an Allotropic Form of Nitrogen.

Previous workers have been attracted by the possibility of liberating nitrogen from hydrazoic acid or its salts in such circumstances as to avoid the disintegration of the triazo-complex and to produce the element in the form of triazo-azoimide,



$$\begin{array}{c}N\\ \|\\ N\end{array}\!\!>N\cdot N<\!\!\begin{array}{c}N\\ \|\\ N\end{array},$$

in which the univalent triazo-group is combined with itself. Szarvasy (Trans., 1900, **77**, 603), for example, electrolysed hydrazoic acid and sodium azide in aqueous solutions of different concentration, obtaining hydrogen, nitrogen, and traces of ammonia; oxidation products of nitrogen did not arise, and although a slight deficiency of nitrogen seemed to indicate some condensation to a polymeric form, determination of density failed to confirm the suggestion. Oxidation of hydrazoic acid by means of potassium permanganate also results in disrupting the triazo-group, but the process has been shown untrustworthy for the gasometric estimation of azoimide (Dennis and Browne, *J. Amer. Chem. Soc.*, 1904, **26**, 577).

It seemed possible, however, that the analogy subsisting between the triazo-complex and the halogens, particularly iodine, might be carried so far as to permit realisation of the following change:

$$C_6H_5\cdot NCl\cdot CO\cdot CH_3 + 2NaN_3 + H_2O = C_6H_5\cdot NH\cdot CO\cdot CH_3 + N_6 + NaCl + NaOH.$$

Accordingly, the action of phenyl acetyl nitrogen chloride on sodium azide was studied under various conditions, with the uniform result that although, in presence of water, liberation of gas occurred, the volume indicated the production of $3N_2$ unmixed with N_6; a solution of the nitrogen halide in dry ether was without action on sodium azide, the substances being recovered unchanged after an interval of five weeks. Perhaps, however, it is well that the attempt to prepare N_6 was not successful, because there is every probability that this form of the element would be highly dangerous; it may even be the case that the alarming explosion which occurred after distilling unsymmetrical bistriazoethane (Trans., 1908, **93**, 1073) originated in liberation of N_6, production of the element in this modification being favoured by the attachment of both triazo-groups to a single atom of carbon. Although the original object of the experiment was not fulfilled, it is possible that the change recorded may form the basis of a method for the quantitative estimation of sodium azide. If interaction takes place in aqueous acetone, the liberation of gas is much more rapid than when the solid phenyl acetyl nitrogen chloride is suspended in aqueous sodium azide, and in less than one hour falls short of the theoretical amount by only 4 or 5 per cent., but the reaction does not appear to be complete even when some excess of the halogen compound is used, since the residual liquid was found to contain sodium azide. Attempts will be made to devise a process by which a weighed quantity of the salt may be led to yield all its nitrogen in elemental form.

Since the completion of the experiments described in this paper, there has appeared a description of the remarkable chloride of azoimide, $Cl\cdot N_3$ (Raschig, *Ber.*, 1908, **41**, 4194), and the method by which this compound was obtained, considered in regard to the action between aqueous sodium azide and phenyl acetyl nitrogen chloride, has a bearing on the mechanism of the change which takes place when the last-named substance liberates iodine from hydrogen iodide. It has been supposed that, when the substituted nitrogen chloride undergoes hydrolysis leading to replacement of chlorine by hydrogen, the halogen escapes in the form of hypochlorous acid (compare Chattaway and Wadmore, Trans., 1902, **81**, 199), but in that case the action of phenyl acetyl nitrogen chloride on aqueous sodium azide should have led to the production of Raschig's chloroazoimide, since that compound arises on acidifying a mixture of sodium hypochlorite and azide with boric or acetic acid. As the nitrogen was, in one set of experiments, collected over potassium hydroxide, in which Raschig has shown the chloroazoimide to be soluble and to regenerate hypochlorite and azide, it would seem that, in this case, at any rate, the action of phenyl acetyl nitrogen chloride in water is distinct from that of hypochlorous acid.

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XXVI.—*The Triazo-group. Part VIII. Azoimides of the Monobasic Aliphatic Acids.*

By Martin Onslow Forster and Robert Müller.

The stability of the triazo-group towards alkali was found to depend, in the case of the azoimides derived from propionic ester, so completely on the position of the substituent that an investigation of the corresponding derivatives of butyric, *iso*butyric, and *iso*valeric acids appeared desirable. Reviewing the series

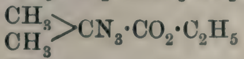
$N_3{\cdot}CO_2{\cdot}C_2H_5$

$N_3{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$

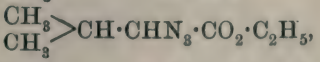
$N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$

$CH_3{\cdot}CHN_3{\cdot}CO_2{\cdot}C_2H_5$

$CH_3{\cdot}CH_2{\cdot}CHN_3{\cdot}CO_2{\cdot}C_2H_5$

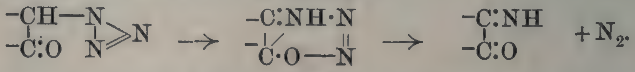


$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CN_3{\cdot}CO_2{\cdot}C_2H_5$



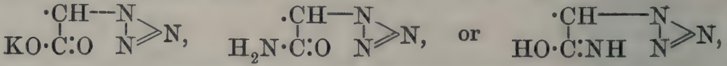
$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{\cdot}CHN_3{\cdot}CO_2{\cdot}C_2H_5,$

it is possible to state precisely the circumstances which determine the behaviour of the triazo-group towards alkalis. Of the substances indicated, triazoformic and β-triazopropionic esters lose hydrazoic acid when treated with potassium hydroxide or ammonia, and do not yield free nitrogen. In contrast with these are the esters of triazoacetic, α-triazopropionic, α-triazobutyric, and α-triazo*iso*valeric acids, which yield the triazo-amides with ammonia, and are hydrolysed to the corresponding triazo-acids by alkali hydroxides; on boiling the alkali salts with excess of the hydroxide, however, nitrogen is eliminated in company with ammonia, whilst hydrazoic acid has never been recognised among the products. α-Triazo*iso*butyric acid alone in the above series appears capable of resisting the attack of alkali in excess, and this is especially noteworthy when it is remembered how readily halogen hydride is removed from the corresponding chloro- and bromo-compounds; there is presented, in fact, a parallel with the resistance of the triazo-group in benzyl azide, which is distinguished from benzyl chloride by indifference towards boiling water or alcoholic potash, a point which gains interest from the general analogy existing in other respects between the triazo-group and the halogens. This immunity from attack is significant also from another standpoint. The ester in question is the only one in which the azoimide-bearing carbon atom of the $N_3 \cdot C \cdot CO$ complex is not hydrogenised, and the suggestion made in an earlier paper to explain the two-thirds nitrogen elimination from α-triazo-ketones (Trans., 1908, **93**, 74) required the presence of at least one atom of hydrogen:



Hence the behaviour of the aliphatic triazo-acids may be regarded as supporting the foregoing explanation.

The escape from attack by alkalis in the *iso*butyric term is even more striking in the case of the amide. While examining the derivatives of triazoacetic and α-triazopropionic acids, it was found that the loss of two-thirds nitrogen is much more rapid from the amides than from the alkali salts; in other words, of the types



the first is least favourable to the change in question; it is the more interesting to find, therefore, that α-triazo*iso*butyramide is merely hydrolysed by boiling alkali, giving ammonia and alkali triazo*iso*butyrate, whilst α-triazobutyramide itself yields torrents of gas when warmed with concentrated potassium hydroxide.

By using the Gaede pump, it has become possible to distil the triazo-acids without risk of explosion, and the appended table summarising the physical properties of these compounds with those of their esters and amides will show them to be well-defined materials, comparable with the unsubstituted acids and their halogen derivatives. Examination of this summary reveals the more conspicuous features of such an homologous series, namely, consecutive diminution of density, and a boiling point for the *iso*butyric term lower than that of the normal isomeride.

Azoimides of the Monobasic Aliphatic Acids.

	Acid.			Ethyl ester.		Amide.
	B. p.	D_{33°.	M. p.	B. p.	D_{20°.	M. p.
Triazoacetic ……	92°/3 mm.	1·3542	16°	45°/3 mm.	1·127	58°
α-Triazopropionic	97·5 /3 mm.	1·2502	0	46 /3 mm.	1·062	79
α-Triazobutyric …	81 /0·17 mm.	1·1519	23·5	63—64 /6·5 mm.	1·038	38—39°
α-Triazo*iso*butyric	75 /0·15 mm.	1·1433	31	52—53 /6·5 mm.	1·0344	93—94
α-Triazo*iso*valeric	82 /0·11 mm.	1·0638	–10	68 /8 mm.	1·0295	79·5°

As regards the explosibility of the triazo-acids, it was to be expected that this would diminish as the series is ascended, the increasing relative importance of the hydrocarbon molecule exerting a damping effect on the disruption force of the triazo-group. It is the more surprising to find, therefore, that, although this relation holds for the acids and esters when heated alone, the decomposition of the latter class by concentrated sulphuric acid exhibits increasing violence with increase of molecular weight, becoming almost explosive in the case of ethyl triazo*iso*butyrate and ethyl triazo*iso*valerate; on the other hand, the liberation of nitrogen by an acid solution of stannous chloride proceeds in the opposite sense, being vigorous with ethyl triazoacetate and very slow with ethyl triazo*iso*valerate.

EXPERIMENTAL.

α-Triazobutyric Acid, $CH_3·CH_2·CHN_3·CO_2H$.

One hundred grams of ethyl α-triazobutyrate were shaken with a 20 per cent. solution of potassium hydroxide containing 36 grams, rise of temperature in the earlier stages of hydrolysis being carefully checked; evolution of nitrogen did not occur, and the clear solution produced after some hours' agitation was extracted twice with ether in order to remove as much alcohol as possible and thereby avoid regeneration of the ester on distilling the acid. The cold solution of potassium triazobutyrate was then decomposed with the calculated amount of 10 per cent. sulphuric acid, saturated with ammonium sulphate, and the product extracted six times with ether, dried with sodium sulphate, and distilled under 0·17 mm. pressure, boiling steadily at 81°:

0·1806 gave 52·1 c.c. N_2 at 16° and 737 mm. N = 32·60.

$C_4H_7O_2N_3$ requires N = 32·55 per cent.

α-Triazobutyric acid crystallises in long, lustrous, snow-white needles melting at 23·5°, and has sp. gr. 1·1519 at 33° compared with water at the same temperature; the liquid rapidly attacks the skin, and has a faint odour which is not disagreeable. It detonates mildly when thrown on a hot plate.

The *silver* salt, precipitated on adding silver nitrate to a solution of ammonium triazobutyrate with one drop of dilute nitric acid, was recrystallised from boiling water, in which it is moderately soluble:

0·1203 gave 0·0735 AgCl. Ag = 45·99.

$C_4H_6O_2N_3Ag$ requires Ag = 45·90 per cent.

The substance forms lustrous, transparent, oblong plates, and becomes violet if exposed to light; when thrown on a hot plate there is not any explosion, and the salt merely deflagrates feebly.

Ethyl a-Triazobutyrate, $CH_3 \cdot CH_2 \cdot CHN_3 \cdot CO_2 \cdot C_2H_5$.—One hundred grams of ethyl a-bromobutyrate, 50 grams of alcohol, and 50 grams of sodium azide were heated on the steam-bath under reflux with enough water to dissolve the salt. After twenty-eight hours, the liquid, originally colourless, had become pale yellow although protected from light, but the product of steam distillation was colourless, weighed 69 grams, and boiled at 63—64° under 6·5 mm. pressure:

0·1706 gave 26·4 c.c. N_2 at 20·7° and 751 mm., along with 0·0185 of ammonia. N = 17·73 as gas, 8·93 as NH_3; total 26·66.

$C_6H_{11}O_2N_3$ requires N = 26·75 per cent.

Ethyl a-triazobutyrate is a colourless oil with a very faint, agreeable perfume, but on inhaling the vapour, especially with steam, it produces a throbbing sensation in the head with palpitation of the heart; it has sp. gr. 1·0380 compared with water at 20°. Although the ester may be hydrolysed by careful treatment with potassium hydroxide, excess of alkali attacks the triazo-group, evolution of nitrogen and ammonia being extremely vigorous if the substance is heated with concentrated potassium hydroxide:

a-Triazobutyramide, $CH_3 \cdot CH_2 \cdot CHN_3 \cdot CO \cdot NH_2$.—When agitated with strong aqueous ammonia the ester dissolved gradually without losing nitrogen, and on concentrating the solution under 20 mm. pressure there separated a pale red oil which solidified after some hours; the dried product was then recrystallised from warm benzene and petroleum:

0·1455 gave 56·0 c.c. N_2 at 20° and 761 mm. N = 44·09.

$C_4H_8ON_4$ requires N = 43·75 per cent.

The amide is freely soluble in alcohol and in water, but dissolves more sparingly in benzene and petroleum, from a mixture of which it crystallises in lustrous, white needles melting at 38—39°; this being a lower temperature than was expected, the preparation of the substance was repeated, with, however, the same result. When covered with concentrated potassium hydroxide, the amide becomes oily and evolves gas, effervescence being very brisk on gently warming the liquid.

Resolution of α-Triazobutyric Acid.

By following the procedure adopted in the case of α-triazopropionic acid, we hoped to arrive easily at the *l*-α-triazobutyric acid, and by reducing this, to ascertain whether the resulting amino-acid is dextrorotatory, like the alanine from triazopropionic acid. The resolution of the triazobutyric acid, however, does not proceed so sharply as in the case of the lower homologue, and although it has been accomplished, the amount of active material at our disposal has only just sufficed to characterise the lævorotatory acid, ester, and amide.

Eighty-two grams of α-triazobutyric acid were added to a paste consisting of 246 grams of brucine with 330 c.c. of water, 200 grams of brucine salt being filtered after twenty-four hours; a 4 per cent. solution of this product in water gave $[\alpha]_D - 36{\cdot}4°$. By successive recrystallisation there was obtained ultimately a fraction having $[\alpha]_D - 42{\cdot}26°$, which was not exceeded by carrying the process another stage, but it weighed only 37 grams; the salt crystallised in long, colourless needles melting at 131°, and decomposed a few degrees above this temperature:

0·3330 gave 34·4 c.c. N_2 at 17° and 756 mm. N = 11·93.

$C_{23}H_{26}O_4N_2,C_4H_7O_2N_3$ requires N = 13·38 per cent.

From this analysis it appears that the substance contains water of crystallisation, a salt with $4H_2O$ requiring 11·76 per cent. of nitrogen.

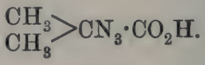
l-α-*Triazobutyric acid* was prepared by decomposing the brucine salt with ammonia, filtering the alkaloid, extracting the solution of ammonium triazobutyrate twice with chloroform, and then decomposing with 20 per cent. sulphuric acid; on adding ammonium sulphate, the active acid was removed after shaking the liquid six times with ether, and remained as a pale yellow oil on evaporating the solvent under reduced pressure without heating. The acid gave $\alpha_D - 60°20'$ in a 1-dcm. tube, and an ethereal solution containing 2·8590 grams, made up to 20 c.c., gave $\alpha_D - 18°6'$ in a 2-dcm. tube, whence $[\alpha]_D - 63{\cdot}3°$.

Ethyl l-*α-triazobutyrate,* obtained on adding slight excess of dry silver oxide to an ethereal solution of the active acid mixed with ethyl iodide, and leaving the substances in association during four days; the liquid was then dried with sodium sulphate, filtered, and evaporated, when the residue distilled to the last drop at 63° under 6 mm. pressure, practically the same temperature, therefore, as the boiling point of the inactive ester. A solution containing 3·1682 grams, made up to 20 c.c. with ether at 21°, gave $\alpha_D - 15°25'$ in a 2-dcm. tube, whence $[\alpha]_D - 48{\cdot}1°$.

l-α-*Triazobutyramide* arose from the ester by the action of concentrated aqueous ammonia, 15 c.c. of which formed a clear solution with 3 grams of the active oil after six hours' agitation; on removing ammonia in a vacuum desiccator, the amide crystallised in long, lustrous needles, moderately soluble in water, freely soluble in acetone and in benzene, but practically insoluble in petroleum. The substance was accordingly recrystallised from the benzene solution by adding petroleum, when silky, snow-white needles separated, melting at 59°. A solution containing 0·2787 gram, made up to 20 c.c. with water, gave α_D 0°51′ in a 2-dcm. tube, whence $[\alpha]_D$ 26·9°; 0·2299 gram, made up to 20 c.c. with acetone, gave α_D 1°5′ in the same tube, whence $[\alpha]_D$ 47·1°.

It was of interest to prepare this compound, because it has been shown that *l*-triazopropionamide (Trans., 1908, **93**, 1863) has a higher melting point than the racemic substance, and, moreover, has, in water and in acetone, rotatory power opposite in sign to that of the acid and the ester from which it is derived. It will be observed that the same relationship associates *l*-α-triazobutyramide with the racemic amide and with *l*-α-triazobutyric acid respectively; the active amide melts 20° higher than the racemic one, and is dextrorotatory in solution. Moreover, it is noteworthy that the summed specific rotatory power of *l*-α-triazopropionic ester (in ether) and its amide (in water), namely, 67·6°, is not widely different from 75°, the corresponding figure in the butyric series; furthermore, in both terms the rotatory power of the amide in acetone is roughly double that observed in water.

α-*Triazo*iso*butyric Acid*,



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CN_3\cdot CO_2H.$$

Proceeding from ethyl α-triazo*iso*butyrate as in the case of the isomeric ester, a quantitative yield of α-triazo*iso*butyric acid was obtained in the form of a colourless oil, which boiled at 75° under 0·15 mm. pressure:

0·1994 gave 58·7 c.c. N_2 at 21° and 750 mm. N = 33·06.
$C_4H_7O_2N_3$ requires N = 32·55 per cent.

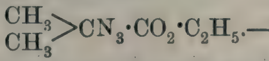
The acid crystallises in centimetre-long, lustrous needles, melting at 31°, and has sp. gr. 1·1433 at 33° compared with water at that temperature; the liquid slowly produces irritating blisters on the skin. Resembling the isomeric substance, it is volatile in steam, and has an odour recalling the fatty acids; this, however, although slightly more pronounced than that of the normal isomeride, is not nearly so disagreeable as the odour of *iso*butyric acid itself. The acid detonates mildly, and takes fire when thrown on a hot plate.

The *silver* salt is not readily soluble in hot water, from which it crystallises in colourless needles:

0·1080 gave 0·0652 AgCl. Ag = 45·44.

$C_4H_6O_2N_3Ag$ requires Ag = 45·76 per cent.

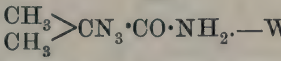
Detonation on a hot plate is very mild.

*Ethyl α-Triazo*iso*butyrate,*  $\frac{CH_3}{CH_3}{>}CN_3\cdot CO_2\cdot C_2H_5$.—The ester was prepared in precisely the same way as the normal ethereal salt, 40 grams of crude material being obtained from 50 grams of ethyl α-bromo*iso*butyrate and 25 grams of sodium azide; under 6·5 mm. pressure it boiled steadily and completely at 52—53°:

0·3043 gave 46·8 c.c. N_2 at 21° and 754 mm., along with 0·03247 of ammonia. N = 17·63 as gas, 8·79 as NH_3; total, 26·47.

$C_6H_{11}O_2N_3$ requires N = 26·75 per cent.

The ester is a colourless, limpid oil, having sp. gr. 1·0344 compared with water at 20°; the odour is much more pronounced than that of the normal isomeride, suggesting peppermint, and the physiological effect of the vapour is also more intense. Twenty per cent. potassium hydroxide hydrolyses the ester very slowly, and the clear solution of potassium α-triazo*iso*butyrate may be boiled vigorously and evaporated to dryness without losing nitrogen and ammonia; moreover, the residue left on evaporation does not contain a trace of alkali azide. The acid is thus distinguished from all the other members of this series.

*α-Triazo*iso*butyramide,*  $\frac{CH_3}{CH_3}{>}CN_3\cdot CO\cdot NH_2$.—When the ester is agitated during several hours with strong aqueous ammonia, the amide separates in large, rectangular plates, often exceeding a centimetre in length:

0·0941 gave 36·2 c.c. N_2 at 21° and 768 mm. N = 44·26.

$C_4H_8ON_4$ requires N = 43·75 per cent.

The substance is much less soluble in water than is the normal modification; it melts at 93—94°, and dissolves freely in alcohol and in warm benzene. Concentrated aqueous potassium hydroxide precipitates the amide from its aqueous solution in lustrous crystals, which redissolve on boiling without liberation of nitrogen; moreover, if the liquid is heated until all ammonia has been removed, dilute sulphuric acid liberates α-triazo*iso*butyric acid, unaccompanied by hydrazoic acid.

*α-Triazo*iso*valeric Acid*, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH\cdot CHN_3\cdot CO_2H$.

The ethyl ester was hydrolysed with the calculated amount of potassium hydroxide, and the liberated acid distilled under 0·11 mm. pressure, when it boiled at 82°:

0·2407 gave 60·3 c.c. N_2 at 15° and 750 mm. N = 28·95.
$C_5H_9O_2N_3$ requires N = 29·37 per cent.

The colourless oil has a very faint odour, which is disagreeable in steam; the sp. gr. is 1·0638 compared with water at 33°. In a freezing mixture of ice and salt, the acid did not solidify on agitation, and was therefore redistilled; nevertheless, it behaved in the same way, and even when immersed in solid carbon dioxide and ether the glassy material did not exhibit crystalline structure, appearing to become fluid again at about – 10°. The acid takes fire on a hot plate, and burns without detonation.

The *silver* salt is very sparingly soluble in boiling water, crystallising in white needles:

0·2070 gave 0·1185 AgCl. Ag = 43·09.
$C_5H_8O_2N_3Ag$ requires Ag = 43·20 per cent.

The substance does not explode when thrown on a hot plate, but merely takes fire.

*Ethyl α-Triazo*iso*valerate*, $\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH\cdot CHN_3\cdot CO_2\cdot C_2H_5$.—The conversion of ethyl α-bromo*iso*valerate into the triazo-compound required a much longer period of interaction than was the case with the lower members of the series. On treating 50 grams of the halogen derivative with sodium azide (25 grams) in the manner already described, the product separated after thirty hours was found to contain a considerable proportion of bromine, and was therefore subjected to the further action of sodium azide (15 grams) during forty hours, after which period halogen could not be detected in the crude triazo*iso*valeric ester. When distilled under 8 mm. pressure, the ethereal salt boiled steadily at 68—68·5°:

0·1330 gave 29·0 c.c. N_2 at 20° and 754 mm. N = 24·74.
$C_7H_{13}O_2N_3$ requires N = 24·56 per cent.

The ester has sp. gr. 1·0295 compared with water at 20°. The odour is pronounced and agreeable, suggesting peppermint, whilst the characteristic effect on the blood pressure is developed in steam. Towards concentrated aqueous potassium hydroxide the substance behaves like ethyl α-triazobutyrate, being rapidly decomposed on heating, with liberation of nitrogen and ammonia; the residue left on evaporation did not contain alkali azide, and the triazo*iso*valeric acid was found to have been completely destroyed.

*a-Triazo*iso*valeramide*, $\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH\cdot CHN_3\cdot CO\cdot NH_2$. — Ethyl α-triazo*iso*valerate is transformed very slowly into the amide when agitated with ammonia, from which the product separates in long, white needles:

0·1000 gave 34·8 c.c. N_2 at 22° and 767 mm. $N = 39{\cdot}81$.

$C_5H_{10}ON_4$ requires $N = 39{\cdot}44$ per cent.

The substance is freely soluble in alcohol and in warm benzene from which it crystallises in long needles melting at 78—79°.

Action of Concentrated Sulphuric Acid on the Triazo-esters.

In the original description of triazoacetic ester (Trans., 1908, **93**, 79) it was stated that the amount of gas evolved when the substance is mixed with concentrated sulphuric acid does not agree with that required by the formula if two-thirds the nitrogen were eliminated, and in dealing with α-triazopropionic ester it was mentioned (page 673) that Mr. Richmond, in elaborating a process for estimating nitrogen in this series, had noted the beneficial effect of alcohol and formaldehyde on the reaction. We have since found that even without these adjuncts it is possible, under suitable conditions, to liberate the two-thirds nitrogen from triazoacetic and triazopropionic esters, and are led to think that the early failures were due to loss of ester by volatilisation consequent on heating the mixture too strongly with sulphuric acid. The results obtained with the homologous esters are tabulated below.

Ester.	Wt. taken.	c.c. N_2.	Temp.	Pressure.	Percentage found.	Percentage calculated.	Character of decomposition.
Triazoacetic ...	0·5533	104·8	25°	767	21·33	21·70	Very sluggish
Triazopropionic	0·4142	69·5	20	765	19·32	19·58	More rapid.
Triazobutyric ...	0·5327	83·7	23	760	17·71	17·83	Very rapid.
Triazo*iso*butyric	0·2548	38·6	20	768	17·52	17·83	Almost explosive.
Triazo*iso*valeric	0·1613	23·0	21	754	16·10	16·37	Almost explosive.

In dealing with the two last members of the series, the acid was admitted in small quantities at a time; if mixed heedlessly, much ester is lost by evaporation, and sulphur dioxide is produced, the stopper being sometimes blown from the vessel. In the case of the first-named substance, the mixture was shaken continuously until no change in volume was observed, and heated meanwhile gently with warm water.

Behaviour of the Esters towards Stannous Chloride dissolved in Hydrochloric Acid.

The solution employed in these experiments contained 20 per cent. of the metal, and the results are as follows.

Ester.	Wt. taken.	c.c. N_2.	Temp.	Pressure.	Percentage found.	Percentage calculated.	Character of decomposition.
Triazoacetic ...	0·3789	70·7	20°	767	21·55	21·70	Vigorous.
Triazopropionic	0·4611	77·5	21	765	19·26	19·58	Smooth and active.
Triazobutyric...	0·5439	85·0	20	759	17·86	17·83	Moderate.
Triazo*iso*butyric	0·2889	41·8	20	766	16·68	17·83	Slow.
Triazo*iso*valeric	0·3696	50·8	21	765	15·75	16·37	Very slow.

In the case of the last-named ester there appeared to be no action for nearly fifteen minutes, when a few small bubbles appeared; the mixture was then heated to about 80°, when decomposition became regular, but was not complete until the vessel had been heated during forty-five minutes in boiling water. The normal triazobutyrate, although decomposed more slowly than the propionate and acetate, gave good results without being heated, but the reduction of the *iso*butyrate is distinctly slower, and is only completed by heating to about 60°.

Derivatives of Triazoacetic Acid.

Triazoacetyl chloride, $N_3{\cdot}CH_2{\cdot}COCl$, was prepared by the action of phosphoryl chloride on sodium triazoacetate suspended in absolute ether. The first attempt consisted in treating the free acid with phosphorus trichloride, when torrents of hydrogen chloride were liberated and the mixture became red, ultimately depositing a red solid; on decanting the clear liquid and removing volatile phosphorus compounds under reduced pressure, a very small quantity of *triazoacetyl chloride* was obtained, boiling at 42° under 15 mm. pressure. In the more successful experiment, 23·7 grams of sodium triazoacetate, which had remained several weeks in the desiccator, were covered with sodium-dried ether and gently warmed with 7·1 grams of phosphoryl chloride; after twelve hours, the filtered solution was evaporated, and distilled under 20 mm. pressure, 5 grams boiling steadily at 50° leaving a viscous, brown oil which probably contained triazoacetic anhydride:

0·3205 gave 0·3830 AgCl. Cl = 29·53.

$C_2H_2ON_3Cl$ requires Cl = 29·68 per cent.

The chloride is a colourless liquid, having the pungent odour of acetyl chloride, and is decomposed immediately by water.

Triazoacetanilide, $C_6H_5 \cdot NH \cdot CO \cdot CH_2 \cdot N_3$, obtained from triazoacetyl chloride and aniline, crystallises from hot water in long, lustrous needles:

0·1009 gave 28·5 c.c. N_2 at 23° and 764 mm. N = 32·01.

$C_8H_8ON_4$ requires N = 31·82 per cent.

The substance is readily soluble in alcohol and in benzene, from which solutions it may be precipitated by water and by petroleum respecttively. The melting point, 83—83·5°, is much lower than might be expected, that of the corresponding chloro-derivative being higher than the melting point of acetanilide itself.

Triazoethyl triazoacetate, $N_3 \cdot CH_2 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot N_3$, arose on mixing triazoacetyl chloride with triazoethyl alcohol in molecular proportion, hydrogen chloride being completely removed after three hours on the water-bath; the product was distilled under 8·5 mm. pressure, when it boiled steadily to the last few drops at 115°:

0·0697 gave 19·6 c.c. N_2 at 18·7° and 753 mm., along with 0·01397 of ammonia. N = 32·53 as gas, 16·51 as NH_3; total 49·04.

$C_4H_6O_2N_6$ requires N = 49·41 per cent.

Triazoethyl triazoacetate is a colourless, limpid oil, which is odourless until warmed. It detonates mildly when thrown on a hot plate, and behaves towards concentrated sulphuric acid and hot potassium hydroxide solution in a manner to be expected from the groups participating in its formation.

An attempt to prepare triazoacetic anhydride was not successful, and, owing to the threatening character of the distillation, was not repeated. Dry sodium triazoacetate was treated with triazoacetyl chloride in presence of a small quantity of ether; after removing undissolved salts, the pale yellow oil was distilled under 1 mm. pressure, when the anhydride boiled at about 113°; but as the residue in the flask rapidly changed into a black tar, the operation was interrupted. The small quantity of anhydride thus obtained was a colourless, heavy, refractive oil without odour, and detonating mildly when thrown on a hot plate; the amount of nitrogen evolved on treatment with concentrated sulphuric acid was 1·4 per cent. below that required by the formula $C_4H_4O_3N_6$; but on admixture with aniline, triazoacetanilide was obtained, melting at 83—83·5°, showing that the principal constituent of the oil was triazoacetic anhydride.

We desire to record our indebtedness to Mr. H. Droop Richmond for the interest taken by him in the analytical difficulties which the

peculiar properties of these compounds have raised; he was also kind enough to estimate the nitrogen in three of the new esters described in this paper.

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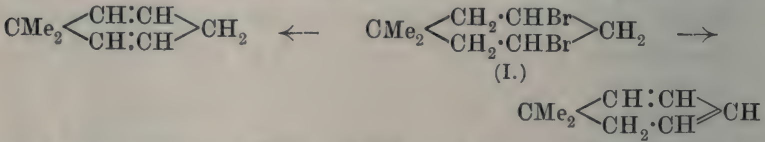
XXVII.—*Nitro-derivatives of ortho-Xylene.*

By Arthur William Crossley and Nora Renouf.

When the mixture of two isomeric dimethyl*cyclo*hexenes, obtained by elimination of two molecules of hydrogen bromide from 3 : 5-dibromo-1 : 1-dimethyl*cyclo*hexane (I), was treated with a nitrating mixture, two substances melting at 115° and 71° were obtained (Trans., 1908, **93**, 646). The methyl groups in the hydrocarbons are both attached to the same carbon atom, and in such cases it has been frequently observed (Trans., 1904, **85**, 264; 1906, **89**, 875) that the transformation into an aromatic substance results in one of the methyl groups wandering into an ortho-position, but never into a meta- or para-position. It was therefore presumed that the above-mentioned substances melting at 115° and 71° were trinitro-*o*-xylenes, a supposition which is now proved to be correct.



$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH{:}CH}\end{matrix}\!>\!\mathrm{CH_2} \longleftarrow \underset{\text{(I.)}}{\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}CHBr}\\ \mathrm{CH_2{\cdot}CHBr}\end{matrix}\!>\!\mathrm{CH_2}} \longrightarrow \mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH{:}CH}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}\!\geqslant\!\mathrm{CH}$$

On consulting the literature of the nitroxylenes, it was found that comparatively little work had been done on the subject. In 1884 Jacobson (*Ber.*, **17**, 160) described 4-nitro-*o*-xylene as a yellow, crystalline substance melting at 29° (b. p. 258°, slight decomposition), obtained by the action of cold fuming nitric acid on *o*-xylene. Later, Noelting and Forel (*Ber.*, 1885, **18**, 2668) found that with a mixture of nitric and sulphuric acids, *o*-xylene gave principally the liquid 3-nitro-*o*-xylene, boiling at 245—247°, but also small quantities of 4-nitro-*o*-xylene.

In a footnote to a paper by Jacobson (*Ber.*, 1886, **19**, 2518), Drossbach stated that *o*-xylene gave di- and tri-nitro-derivatives only when heated with a nitrating mixture for some time above 100°; the dinitro-*o*-xylene melted at 71°, and the trinitro-*o*-xylene at 178°.

Lastly, Noelting and Thesmar (*Ber.*, 1902, **35**, 628) obtained by the further nitration of 4-nitro-*o*-xylene, 4 : 5-dinitro-*o*-xylene (m. p. 115—116°) and 4 : 6-dinitro-*o*-xylene (m. p. 75—76°). They considered it most probable that Drossbach's dinitro-*o*-xylene, melting at 71°, was 4 : 6-dinitroxylene, but it follows from the experiments now described that, as Drossbach prepared his dinitroxylene at a temperature above 100°, it would in reality be 3 : 4 : 6-trinitro-*o*-xylene, melting at 72°. Noelting and Thesmar further proved that Drossbach's trinitroxylene (m. p. 178°) was trinitro-*m*-xylene, due to the *o*-xylene with which he worked containing *m*-xylene.

These authors state "that ortho-xylene is incapable of yielding a trinitro-derivative, even under the influence of the most energetic nitrating agents." They arrived at this conclusion as the result of nitrating 4-nitro-*o*-xylene with a mixture of fuming nitric and sulphuric acids, allowing the temperature to rise as high as 150°, when "the reaction product contained no trace of a trinitro-derivative, which should have been easily recognised by means of its sparing solubility in alcohol; but the mixture consisted exclusively of the two above-mentioned dinitro-*o*-xylenes, melting respectively at 115—116° and 75—76°."

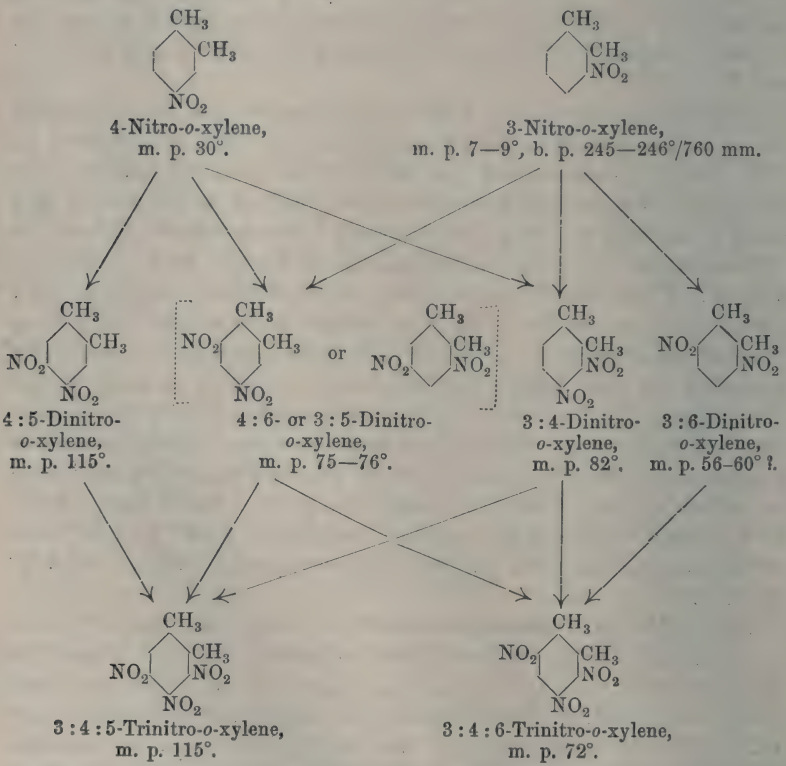
Despite this statement of Noelting and Thesmar, the present authors felt so certain regarding the nature of the two substances melting at 115° and 71°, obtained by the action of a nitrating mixture on dimethyl*cyclo*hexene, that *o*-xylene was nitrated under exactly the same conditions, and was found to yield the same two substances melting at 115° and 72°, and which analysis showed to be trinitro-*o*-xylenes. These two trinitro-*o*-xylenes are so similar in melting point, crystalline form, and solubility in alcohol to the dinitro-*o*-xylenes melting repectively at 115° and 75° that they might easily be mistaken for them (although there is no possibility of error if the mixed melting points are taken), and these are probably the reasons that led Noelting and Thesmar to make the above-quoted erroneous statement, for when 4-nitro-*o*-xylene is nitrated under the conditions employed by these authors, the resulting product would undoubtedly be a mixture of the trinitro-*o*-xylenes melting at 115° and 72°, and would contain no trace of the dinitro-*o*-xylenes melting at 115° and 75°.

It was decided to attempt the orientation of the two trinitro-*o*-xylenes, and as the simplest way to attain this end seemed to be a study of the further nitration products of the mono- and di-nitro-*o*-xylenes, this work has been carried out, with the result that all the possible mono-, di-, and tri-nitro-*o*-xylenes are now described. The only one about which any doubt exists is 3 : 6-dinitro-*o*-xylene. It is produced by the further nitration of 3-nitro-*o*-xylene, but in such very small amount that it has not been possible thoroughly to investigate its properties, which it is hoped to describe more accurately when experiments, now in progress, with large quantities of material are completed.

According to theory there should exist two mononitro-*o*-xylenes, four dinitro-*o*-xylenes, and two trinitro-*o*-xylenes.*

4-Nitro-*o*-xylene, melting at 30°, was prepared and correctly orientated by Jacobson (*loc. cit.*); but as a further proof of its constitution, it has now been oxidised with dilute nitric acid, when it gives a quantitative yield of 4-nitrophthalic acid.

3-Nitro-*o*-xylene, which Noelting and Forel did not isolate in a pure condition, is a faintly yellow liquid boiling at 245—246°/760 mm. As it is not identical with 4-nitro-*o*-xylene, and as there can be but two mononitro-*o*-xylenes, its constitution really requires no further proof; but it has also been oxidised with dilute nitric acid, when it gives a quantitative yield of 3-nitrophthalic acid.


4-Nitro-o-xylene, m. p. 30°.
3-Nitro-o-xylene, m. p. 7—9°, b. p. 245—246°/760 mm.
4 : 5-Dinitro-o-xylene, m. p. 115°.
or
4 : 6- or 3 : 5-Dinitro-o-xylene, m. p. 75—76°.
3 : 4-Dinitro-o-xylene, m. p. 82°.
3 : 6-Dinitro-o-xylene, m. p. 56–60° ?.
3 : 4 : 5-Trinitro-o-xylene, m. p. 115°.
3 : 4 : 6-Trinitro-o-xylene, m. p. 72°.

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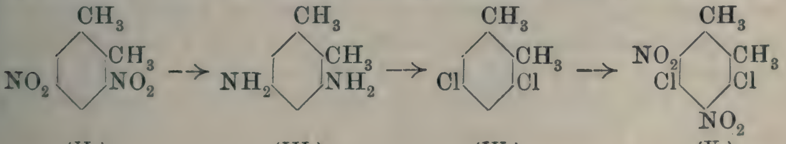
* The argument used in the orientation of the nitro-*o*-xylenes will be more readily understood by referring to the diagrammatic formulæ above.

When 4-nitro-*o*-xylene is further nitrated, it should yield three dinitro-derivatives, namely, 4 : 5-, 4 : 6-, and 3 : 4-dinitro-*o*-xylenes, and this has been proved to be the case, the three derivatives melting respectively at 115°, 75°, and 82°. Of these three dinitro-*o*-xylenes, one, namely, 4 : 5-dinitro-*o*-xylene, should only be capable of being produced from the 4-nitro-*o*-xylene, and theory is again substantiated by experiment, for the dinitro-*o*-xylene melting at 115° is only obtained from 4-nitro-*o*-xylene; no trace of it has in any case been isolated by the further nitration of 3-nitro-*o*-xylene. The substance melting at 115° must therefore be 4 : 5-dinitro-*o*-xylene, which constitution was assigned to it by Noelting and Thesmar (*loc. cit.*) from a study of its reduction products, and it may, therefore, on both these grounds be assumed to be correct.

Further, the dinitro-*o*-xylene melting at 75° was also prepared by Noelting and Thesmar by nitration of 4-nitro-*o*-xylene, and, again, from a study of its reduction products these authors concluded that it was 4 : 6-dinitro-*o*-xylene. The correctness of this conclusion has now been demonstrated in the following manner.

In 1904 (Trans., **85**, 284) one of the present authors described 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene, the constitution of which substance was established beyond doubt. Now if the dinitro-*o*-xylene melting at 75° is 4 : 6-dinitro-*o*-xylene, it should be converted into 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene by chlorination; but although it was not found possible directly to chlorinate the dinitro-*o*-xylene melting at 75°, it was ultimately converted into the above dichlorodinitro-*o*-xylene by the following method.

3 : 5(or 4 : 6-)-Dinitro-*o*-xylene (II)* was reduced with tin and hydrochloric acid, and the resulting diamine (III) diazotised and treated with cuprous chloride, thus yielding 3 : 5-dichloro-*o*-xylene (IV), which on nitration gave 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene (V), identical with the dichlorodinitro-*o*-xylene described in 1904.



(II.) (III.) (IV.) (V.)

The constitutions of two out of the three possible dinitro-*o*-xylenes obtainable by the further nitration of 4-nitro-*o*-xylene are thus definitely established, and it therefore follows that the third isomeride melting at 82° must be 3 : 4-dinitro-*o*-xylene.

Again, 3-nitro-*o*-xylene should, like 4-nitro-*o*-xylene, yield three dinitro-derivatives on further nitration, and such is found to be the case. Of these three dinitro-*o*-xylenes, one should only be producible from 3-nitro-*o*-xylene, and experiment shows this to be the dinitro-*o*-xylene melting at 56—60°, of which substance no trace could be obtained by the further nitration of 4-nitro-*o*-xylene, and it must therefore be 3 : 6-dinitro-*o*-xylene.

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* 4 : 6-Dinitro-*o*-xylene may also be designated 3 : 5-dinitro-*o*-xylene, since the 3 : 5- and 4 : 6-positions are identical.

The other two isomerides should be 3 : 4- and 3 : 5(4 : 6-)-dinitro-*o*-xylenes, which supposition proves to be correct, for the dinitro-*o*-xylenes isolated melt at 82° and 75°, and are identical with the substances of similar melting points obtained from the further nitration of 4-nitro-*o*-xylene.

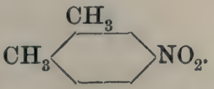
The constitutions of the trinitro-*o*-xylenes follow from those of the dinitro-*o*-xylenes, for 4 : 5-dinitro-*o*-xylene can only give one trinitro-*o*-xylene, and it does, namely, the one melting at 115°, which must therefore be 3 : 4 : 5-trinitro-*o*-xylene, and the second trinitro-*o*-xylene melting at 72° must therefore be 3 : 4 : 6-trinitro-*o*-xylene. If this argument is correct, then 3 : 6-dinitro-*o*-xylene should give on further nitration only 3 : 4 : 6-trinitro-*o*-xylene, and 4 : 6(3 : 5-)-dinitro- and 3 : 4-dinitro-*o*-xylenes should give on further nitration mixtures of the two possible trinitro-*o*-xylenes, and, again, theoretical requirements have been established by experiment.

One point of practical interest is worth while calling attention to, namely, the use of concentrated sulphuric acid as an agent for the separation of the isomeric nitro-*o*-xylenes. If, for example, the crude mixture of trinitro-*o*-xylenes is dissolved in about six times its weight of concentrated sulphuric acid, heating to as low a temperature as possible so as to ensure solution, then, on cooling, a large fraction of pure 3 : 4 : 5-trinitro-*o*-xylene (m. p. 115°) separates out. The solid obtained by pouring the sulphuric acid liquor into water is crystallised from absolute alcohol, when pure 3 : 4 : 6-trinitro-*o*-xylene (m. p. 72°) is obtained. On evaporating the alcoholic mother liquor and repeating this alternate treatment with sulphuric acid and then alcohol, a complete separation of the two trinitro-*o*-xylenes may be effected.

Moreover, the method may be applied with equal success to the isomeric dinitro-*o*-xylenes, only in this case it is sometimes necessary to add a few drops of water to the sulphuric acid before crystallisation will take place. For example, of the two dinitro-*o*-xylenes melting at 115° and 75°, the former crystallises from sulphuric acid and the latter does not, and a separation of the two substances is thus comparatively easily carried out; whereas Noelting and Thesmar, who first prepared this mixture of dinitro-*o*-xylenes, separated them by "a series of fractional crystallisations from alcohol." It follows, however, that there is a considerable loss of material during the various filtrations and evaporations necessitated by the process, especially with the dinitro-*o*-xylenes; but even then the method gives better results than fractionation from alcohol, by which means alone it is practically impossible to separate in appreciable quantity the three dinitro-*o*-xylenes produced by further nitration of either of the mononitro-*o*-xylenes.

EXPERIMENTAL.

4-*Nitro*-o-*xylene*,



4-*Nitro*-o-*xylene* is best obtained by the action of a mixture of nitric and acetic acids on *o*-xylene as described on page 216, when the yield of pure substance is 11—12 grams from 50 grams of *o*-xylene. It is readily soluble in the cold in the usual organic solvents, and crystallises from absolute alcohol in long, transparent, glistening, yellow prisms, melting at 30°, and possessing a marked odour resembling that of nitrobenzene. It boils at 254°/748 mm. with very slight decomposition, and without any sign of decomposition at 143°/21 mm:

0·1924 gave 15·2 c.c. N_2 (moist) at 13° and 746 mm. $N = 9·16$.

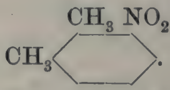
$C_8H_9O_2N$ requires $N = 9·27$ per cent.

Jacobson (*loc. cit.*) recommended the treatment of *o*-xylene with eight to ten times its weight of nitric acid for the preparation of 4-nitro-*o*-xylene, but it is now found that even with eight times the weight of nitric acid the yield of mononitro-*o*-xylenes is only one-half what may be obtained when *o*-xylene is nitrated with six times its weight of fuming nitric acid, and even under these latter conditions the yield is not so good as with nitric and acetic acids.

Jacobson further states that 4-nitro-*o*-xylene is the only mononitro-*o*-xylene produced in appreciable quantity by the action of fuming nitric acid on *o*-xylene, whilst Noelting and Forel say that they obtained only a small amount of the liquid 3-nitro-*o*-xylene by this method. As a matter of fact, the two mononitro-*o*-xylenes are produced in approximately equal amount.

Oxidation of 4-*Nitro*-o-*xylene.*—One gram of 4-nitro-*o*-xylene was heated with 10 c.c. of nitric acid (sp. gr. 1·15) in a sealed tube for six hours at 170—180°. The resulting clear liquid was evaporated on the water-bath, when the residual solid (1·4 grams; theory 1·4 grams) melted at 162—164°, and, after one crystallisation from water saturated with hydrogen chloride, it separated in microscopic, transparent scales melting at 165°. Miller (*Annalen*, 1881, **208**, 230) gives the melting point of 4-nitrophthalic acid as 161°, and the melting point of the anhydride, prepared by sublimation of the acid, as 114°. The anhydride of the above-mentioned specimen of the acid was prepared by heating with acetyl chloride, and crystallising the residue from a mixture of chloroform and light petroleum (b. p. 40—60°), when it separated in clusters of colourless, leaf-like needles melting at 119°. It is insoluble in light petroleum, and readily soluble in the cold in the usual organic media with the exception of ether.

3-*Nitro*-o-*xylene*,



3-*Nitro*-o-*xylene* is produced in largest amount by the action of a mixture of sulphuric and fuming nitric acids on *o*-xylene (compare page 216), when the yield of pure material is 25 grams from 50 grams of *o*-xylene:

0·2540 gave 19·8 c.c. N_2 (moist) at 14° and 758 mm. N = 9·15.

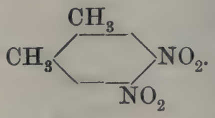
$C_8H_9O_2N$ requires N = 9·27 per cent.

It is a clear, pale yellow, refractive oil boiling at 131°/20 mm., and at 245—246°/760 mm. without any sign of decomposition.

Noelting and Forel (*loc. cit.*, p. 2673) state that their specimen of 3-nitro-*o*-xylene contained a certain quantity of the solid 4-nitro-*o*-xylene, although it remained completely liquid at −20°. When 3-nitro-*o*-xylene is cooled in a freezing mixture, and the sides of the containing vessel scratched with a glass rod, it solidifies readily to a pale yellow solid which melts at +7—9°.

Oxidation of 3-*Nitro*-o-*xylene.*—One gram of 3-nitro-*o*-xylene was heated with 10 c.c. of nitric acid (sp. gr. 1·15) in a sealed tube for four hours at 170—180°. The resulting clear green liquid was evaporated on the water-bath, when 1·4 grams (theory 1·4) of a solid were obtained, which crystallised from water in yellow, transparent prisms melting at 217° with evolution of gas, and, after resolidification, at 163—164°. Miller (*Annalen*, 1881, **208**, 240) gives 217—218° as the melting point of 3-nitrophthalic acid, and Graeff (*Ber.*, 1882, **15**, 1127) gives the melting point of the anhydride as 163—164°. The anhydride of the above specimen of the acid was prepared by heating with acetyl chloride and crystallising the resulting solid from benzene, when it separated in sheaves of slender needles melting at 163°.

4 : 5-*Dinitro*-o-*xylene*,



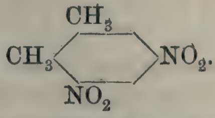
4 : 5-*Dinitro*-o-*xylene*, obtained by the further nitration of 4-nitro-*o*-xylene with a mixture of nitric and sulphuric acids (compare page 212), is sparingly soluble in light petroleum, and readily so in the cold in the

usual organic solvents, except alcohol, from which it crystallises in long, white, glistening needles melting at 115°. It also crystallises from concentrated or slightly diluted sulphuric acid in glistening needles:

0·1115 gave 14 c.c. N_2 (moist) at 17° and 760 mm. N = 14·57.
$C_8H_8O_4N_2$ requires N = 14·29 per cent.

When mixed with trinitro-*o*-xylene melting at 115°, it melts at 82—83°, becoming quite clear at 86°.

4 : 6-*Dinitro*-o-*xylene*,



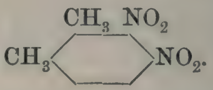
4 : 6-*Dinitro*-o-*xylene* is produced in largest amount by the action of fuming nitric acid on xylene at a temperature of 22—25° (compare page 216, experiment II):

0·1409 gave 16·8 c.c. N_2 (moist) at 13° and 762 mm. N = 14·13.
$C_8H_8O_4N_2$ requires N = 14·29 per cent.

It is readily soluble in the cold in chloroform, ethyl acetate, benzene, or acetone, and crystallises from alcohol in very faintly yellow, stout, leafy needles, or on slow crystallisation in long, transparent needles. When once in a moderately pure condition, it crystallises from a mixture of chloroform and light petroleum (b. p. 40—60°) in stellar aggregates of long, glistening needles, showing, when heated in a capillary tube, a distinct shrinkage in bulk at 71°, and melting at 75—76°. When mixed with 3 : 4 : 6-trinitro-*o*-xylene (m. p. 72°), it melts at 45—46°, becoming quite clear at 63°. 4 : 6-Dinitro-*o*-xylene does not crystallise from concentrated sulphuric acid.

Conversion into 3 : 5-*Dichloro*-4 : 6-*dinitro*-o-*xylene*. — Attempts directly to chlorinate 4 : 6-dinitro-*o*-xylene failed, and the following method was therefore adopted for the preparation from it of 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene. Ten grams of 4 : 6-dinitro-*o*-xylene were reduced with tin and hydrochloric acid, and 3 grams of the resulting base dissolved in hydrochloric acid, a solution of 6 grams of cuprous chloride in hydrochloric acid added, the whole heated on the water-bath to 60—70°, and a solution of 4 grams of sodium nitrite in 20 c.c. of water gradually added. After standing one hour, the mixture was distilled in a current of steam, when a slightly coloured oil passed over, which was extracted with ether, the ethereal solution washed with sodium hydroxide solution, dried, and the ether evaporated. The resulting oil (1·3 grams) was directly nitrated by adding it to a mixture of 12 c.c. of one volume of fuming nitric acid and two volumes of sulphuric acid. Solid separated almost at once, and, after heating on the water-bath for half an hour, the whole was poured into water and the resulting solid (1·7 grams) crystallised from absolute alcohol, when it separated in colourless, glistening, four-sided plates melting at 176°. On admixture with 3 : 5-dichloro-4 : 6-dinitro-*o*-xylene (Trans., 1904, **85**, 284), the melting point remained unaltered, thus proving the identity of the two substances.

3 : 4-*Dinitro*-o-*xylene*,



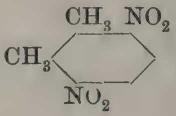
3 : 4-*Dinitro*-o-*xylene* is best prepared by the action of fuming nitric acid on *o*-xylene at 22—25° (compare page 216, experiment II):

0·1016 gave 12·6 c.c. N_2 (moist) at 14° and 740 mm. N = 14·20.

$C_8H_8O_4N_2$ requires N = 14·29 per cent.

It is readily soluble in the cold in the ordinary organic media, except light petroleum and alcohol, from which latter solvent it crystallises in small, silken needles melting at 82°. It also crystallises from concentrated or slightly diluted sulphuric acid. When mixed with 4 : 6-dinitro-*o*-xylene, it melts at 46—48°, becoming quite clear at 58°, and when mixed with 4 : 5-dinitro-*o*-xylene it melts at 64—65°, becoming clear at 83°.

3 : 6-*Dinitro*-o-*xylene*,



3 : 6-*Dinitro*-o-*xylene* is obtained by the further nitration of 3-nitro-*o*-xylene with fuming nitric acid (compare page 214):

0·1010 gave 12·2 c.c. N_2 (moist) at 11° and 754 mm. N = 14·28.

$C_8H_8O_4N_2$ requires N = 14·29 per cent.

It is extremely soluble in the cold in the usual organic solvents except light petroleum and alcohol, in which latter solvent it is, however, much more soluble than any of the other isomeric dinitro-*o*-xylenes, and from which it crystallises in colourless, fern-like aggregates melting at 56—60°. Although separating in detached crystals, these mat together on filtering and form a waxy substance, a property also exhibited by 3 : 5-dichloro-4-bromo-*o*-xylene (Trans., 1904, **85**, 275).

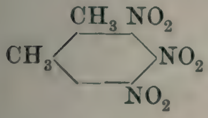
This dinitro-*o*-xylene was only isolated in minute quantities. Much larger amounts of material are now being worked up, and it is hoped that a more accurate description of its properties will be published at no distant date.

Trinitro-o-*xylenes.*

Twenty grams of *o*-xylene were slowly added to 200 c.c. of a mixture of one part nitric acid (sp. gr. 1·5) and two parts of concentrated sulphuric acid, the whole being cooled in tap-water. The partly-nitrated *o*-xylene separated as an oil, which floated on the acid mixture, and the whole was therefore heated on the water-bath for fifteen hours with frequent shaking, poured into water, extracted with ether, the ethereal solution washed with sodium hydroxide solution,* then with water, dried, and the ether evaporated. The solid residue (31 grams) was dissolved in 180 c.c. of concentrated sulphuric acid and allowed to stand, when 6·5 grams separated, in which the nitrogen was determined after crystallisation from alcohol:

0·1094 gave 16·6 c.c. N_2 (moist) at 17° and 750 mm. N = 17·37.

$C_8H_7O_6N_3$ requires N = 17·43 per cent.

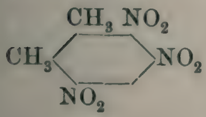


3 : 4 : 5-*Trinitro*-o-*xylene* is readily soluble in the cold in chloroform, benzene, ethyl acetate, or acetone, fairly readily soluble in alcohol on warming, and separates on cooling in long, colourless needles melting at 115°. The sulphuric acid mother liquor was then poured into water, and the separated solid (22 grams) crystallised from alcohol, when 14 grams were obtained and analysed after a second crystallisation:

0·1412 gave 0·2050 CO_2 and 0·0423 H_2O. C = 39·59; H = 3·32.

0·1230 ,, 18·6 c.c. N_2 (moist) at 18° and 756 mm. N = 17·37.

$C_8H_7O_6N_3$ requires C = 39·83; H = 2·90; N = 17·43 per cent.



3 : 4 : 6-*Trinitro*-o-*xylene* is readily soluble in the cold in the ordinary organic solvents, except light petroleum and alcohol, in which latter liquid it dissolves readily on warming, separating in clusters of faintly yellow, glistening, flattened needles melting at 72°. It does not crystallise from concentrated sulphuric acid, and on exposure to light gradually darkens in colour to a decided yellow.

The alcoholic mother liquors from the 3 : 4 : 6-trinitro-*o*-xylene were evaporated, and the residue again nitrated by heating for three hours with 60 c.c. of a similar nitrating mixture to that originally employed, and worked up exactly as described above, when a further 0·8 gram of 3 : 4 : 5-trinitro-*o*-xylene and 2·4 grams of 3 : 4 : 6-trinitro-*o*-xylene were obtained. Thus 20 grams of *o*-xylene give under these conditions 7·3 grams of 3 : 4 : 5-trinitro-*o*-xylene and 16·4 grams of 3 : 4 : 6-trinitro-*o*-xylene.

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* The washings from this process were coloured deep brown (compare Noelting and Forel), but the nature of the product contained in the solution has not so far been further investigated.

A number of experiments were carried out on the nitration of *o*-xylene by heating to the boiling point of the mixture on a sand-bath. In all cases the trinitro-derivatives were produced in approximately the same amounts, no matter whether the heating was continued for only one hour or for twenty-five hours, the smallest quantities being 5·7 grams of 3 : 4 : 5-trinitro-*o*-xylene and 14·5 grams of 3 : 4 : 6-trinitro-*o*-xylene when heating was continued for twenty-five hours.

In none of these experiments was any evidence of the existence of a tetranitro-*o*-xylene obtained.

*Further Nitration of the Mono- and Dinitro-*o*-xylenes.*

Nitration of 4-*Nitro*-o-*xylene*.—Twenty grams of 4-nitro-*o*-xylene were treated with a mixture of nitric and sulphuric acids exactly as described by Noelting and Thesmar (*loc. cit.*, p. 631). As soon as all the nitrating mixture had been added, solid commenced to separate, which disappeared during the ten minutes' heating, but separated again on cooling.* The whole was poured into water, allowed to stand until clear, the solid (24 grams) filtered, dried on porous plate, and dissolved, with the aid of as little heat as possible, in 120 c.c. of concentrated sulphuric acid. Sometimes it was found necessary to add a few drops of water to cause crystallisation, but in this experiment, without the addition of any water, 3·9 grams of solid were obtained melting at 107—112°, and after one crystallisation from alcohol at 115°, and which was proved by the mixed melting-point method to be 4 : 5-dinitro-*o*-xylene. On addition of a little water to the sulphuric acid mother liquor, a further 1·4 grams of this same dinitro-*o*-xylene separated, melting at 100—107°, and after recrystallisation from alcohol at 115°.

The sulphuric acid solution was then poured into water and the resulting solid (17·5 grams) crystallised from alcohol, when 8·5 grams of 4 : 6-dinitro-*o*-xylene (m. p. 75°) were isolated. The alcoholic mother liquor was then evaporated, the residue again dissolved in concentrated sulphuric acid, and the whole process repeated. The first fraction from sulphuric acid consisted of

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* Some of this solid was crystallised from alcohol, when it melted at 115°. This fact suggested that the dinitro-*o*-xylene melting at 115° would crystallise from sulphuric acid, which was found to be the case, and this explains the use of concentrated sulphuric acid as a crystallising agent so frequently referred to in this communication.

4 : 5-dinitro-*o*-xylene, and the later ones, after repeated fractional crystallisation from alcohol, were proved to consist of 4 : 5-dinitro-*o*-xylene mixed with a very small quantity of 3 : 4-dinitro-*o*-xylene (m. p. 82°).

The sulphuric acid mother liquor on pouring into water, etc., gave a further quantity of 4 : 6-dinitro-*o*-xylene (m. p. 75°).

4-Nitro-*o*-xylene was then further nitrated by gradually adding three times its weight of fuming nitric acid to the powdered substance, cooling when necessary. It was allowed to stand one hour at the ordinary temperature, poured into water, extracted with ether, the ethereal solution washed with sodium hydroxide solution, then with water, dried, and the ether evaporated. The residue was worked up as described in the previous experiment, when there was obtained a smaller proportion of 4 : 6-dinitro-*o*-xylene, but a much larger amount of material insoluble in sulphuric acid, than when 4-nitro-*o*-xylene was nitrated with nitric and sulphuric acids. This material consisted of a mixture of 4 : 5-dinitro-*o*-xylene and 3 : 4-dinitro-*o*-xylene, which melts constantly at 62—65°, becoming quite clear some degrees higher. A separation of its constituents can only be effected by repeated fractional crystallisation from large volumes of alcohol, and the process is not, therefore, to be recommended for the preparation of either of these dinitro-*o*-xylenes. The reaction was investigated in this case solely to ascertain the nature of the further nitration products of 4-nitro-*o*-xylene. 4 : 5-Dinitro-*o*-xylene is best prepared by the action of nitric and sulphuric acids on 4-nitro-*o*-xylene, as under these conditions there is so little 3 : 4-dinitro-*o*-xylene (m. p. 82°) produced that the major portion of the 4 : 5-dinitro-*o*-xylene can be isolated without difficulty. On the other hand, 3 : 4-dinitro-*o*-xylene is most conveniently produced in large quantities by the nitration of *o*-xylene with nitric acid at 22—25° (compare page 216).

*Nitration of 3-Nitro-*o*-xylene.*—Five grams of 3-nitro-*o*-xylene were treated with a mixture of nitric and sulphuric acids as described by Noelting and Thesmar for the nitration of 4-nitro-*o*-xylene (*loc. cit.*). These authors state (p. 633) that when 3-nitro-*o*-xylene is nitrated with a mixture of nitric and sulphuric acids, "the reaction product appears to be of a complex nature, as its melting point is hardly above 0°." The latter part of this statement is not correct, for the mixture of dinitro-*o*-xylenes, produced under the above conditions, solidified readily (5·2 grams) on pouring into water. It was treated alternately with sulphuric acid and then alcohol, as described on p. 212 (nitration of 4-nitro-*o*-xylene), when 1·6 grams of 3 : 4-dinitro-*o*-xylene were isolated from the sulphuric acid treatment, and 1·1 grams of 3 : 5(4 : 6-)-dinitro-*o*-xylene from alcohol. The residue from evaporation of the alcohol melted at a low temperature, and had a waxy consistency, suggesting the presence of a third isomeride, which was eventually isolated in very small amount from the product of the action of nitric acid alone on 3-nitro-*o*-xylene.

For this purpose, 20 grams of 3-nitro-*o*-xylene were treated with 40 c.c. of fuming nitric acid, employing exactly the conditions and method of working up the product as described under the action of nitric acid on 4-nitro-*o*-xylene (compare page 213). The first treatment with sulphuric acid gave 4·2 grams of 3 : 4-dinitro-*o*-xylene (m. p. 82°), and subsequent treatment with alcohol 3·3 grams of 3 : 5-dinitro-*o*-xylene (m. p. 75°). The process of further separation with sulphuric acid and then alcohol was twice repeated, when the alcoholic solutions gave further quantities of 3 : 5-dinitro-*o*-xylene. The fractions obtained from sulphuric acid were all of a more or less waxy nature, and by repeated fractional crystallisation from alcohol, they yielded very small quantities of 3 : 4-dinitro-*o*-xylene and the fourth isomeride, namely, 3 : 6-dinitro-*o*-xylene, melting at 56—60°. The yield of the latter is small, less than 1 gram being isolated in an approximately pure state.

Nitration of 4 : 5-*Dinitro*-o-*xylene.*—One gram of 4 : 5-dinitro-*o*-xylene was heated on the water-bath for two hours with 30 c.c. of a mixture of 1 volume of fuming nitric acid and 2 volumes of sulphuric acid. On cooling, solid separated, but the whole was poured into water and filtered, when 1 gram of solid, melting at 111—113°, was obtained, which, after crystallisation from alcohol, melted sharply at 115°. When mixed with 3 : 4 : 5-trinitro-*o*-xylene (m. p. 115°), the melting point was unaltered, but when mixed with 4 : 5-dinitro-*o*-xylene it melted at 83—86°. Thus, the sole product of nitrating 4 : 5-dinitro-*o*-xylene is 3 : 4 : 5-trinitro-*o*-xylene.

Nitration of 4 : 6-*Dinitro*-o-*xylene.*—Under similar conditions to the last experiment, 1 gram of 4 : 6-dinitro-*o*-xylene gave 0·6 gram of nitration product, from which were isolated 0·25 gram of 3 : 4 : 5-trinitro-*o*-xylene and 0·2 gram of 3 : 4 : 6-trinitro-*o*-xylene.

Nitration of 3 : 4-*Dinitro*-o-*xylene.*—Three grams of 3 : 4-dinitro-*o*-xylene, nitrated as above described, gave 3·4 grams of a product, which yielded 0·4 gram of 3 : 4 : 5-trinitro-*o*-xylene and 2·3 grams of 3 : 4 : 6-trinitro-*o*-xylene.

Nitration of 3 : 6-*Dinitro*-o-*xylene.*—When nitrated in the same manner, 0·5 gram of 3 : 6-dinitro-*o*-xylene gave only 3 : 4 : 6-trinitro-*o*-xylene, melting at 72°.

Action of Nitric Acid on o-*Xylene.*

Experiment I.—Three hundred grams of fuming nitric acid were cooled to – 16°, and 50 grams of *o*-xylene added drop by drop, care being taken that the temperature did not rise above – 4° : an operation that lasted about one and a-half hours. A second quantity of 50 grams of *o*-xylene was treated in a similar manner, and the resulting liquids poured into water, extracted with ether, the ethereal solution washed with sodium hydroxide solution, then with water, dried, and, after evaporation of the ether, the residue was distilled under 36 mm. pressure, when the following fractions were obtained, none of which showed the slightest sign of decomposition during distillation :

150—155° = 14·4 grams.
155—170 = 27·0 ,,
170—185 = 20·0 ,,
185—195° = 6·0 grams.
195—200 = 3·5 ,,
200—213 = 60 0 ,,

The fractions boiling below 195° were redistilled at 26 mm. :

135—140° = 3·0 grams.
140—145 = 5·4 ,,
145—147 = 12·8 ,,
147—150 = 15·0 ,,
150—155° = 12·0 grams.
155—165 = 4·2 ,,
165—190 = 3·9 ,,
Residue = 7·5 ,, (A).

Each of these fractions was separately cooled in a freezing mixture and then filtered, using an ice funnel, and the residue spread on porous plate, when 8·6 grams of a yellow solid remained, which, after one crystallisation from alcohol, melted sharply at 30° (4-nitro-*o*-xylene). The porous plate was extracted with ether, the filtrate from the various fractions added to the ethereal solution, the latter dried, the ether evaporated and the residue again fractioned in a vacuum, and the whole process repeated four times, when 18 grams of pure 4-nitro-*o*-xylene were isolated.

The filtrate from the 4-nitro-*o*-xylene became much more constant in boiling point, and finally yielded 19 grams of pure 3-nitro-*o*-xylene and 7 grams of a mixture of the two mononitro-*o*-xylenes, which was added to similar fractions obtained in other experiments and the separation process repeated. Thus 44 grams out of the 57 grams of liquid obtained from the second of the fractionations detailed above are accounted for, the loss being very small when taking into consideration the number of operations through which it has to pass.

The residue A (7·5 grams) solidified entirely, and was added to the solid fractions 195—200° and 200—213°, and the whole (71 grams) dissolved in 213 c.c. of concentrated sulphuric acid and worked up for the separation of the dinitro-*o*-xylenes by alternate treatment with sulphuric acid and then alcohol, as described on page 212. In this way there were obtained 18·5 grams of 3 : 4-dinitro-*o*-xylene, 17·5 grams of 4 : 6-dinitro-*o*-xylene, 0·3 gram of 4 : 5-dinitro-*o*-xylene, 5 grams of the mixture of 4 : 5-dinitro-*o*-xylene and 3 : 4-dinitro-*o*-xylene melting at 63—65° (compare page 210), and 10·3 grams of a low melting, waxy solid, which consisted of all four dinitro-*o*-xylenes, its waxy nature being due to the presence of 3 : 6-dinitro-*o*-xylene. As it proved impossible to separate further this mixture of four substances, it and all similar residues from other experiments were converted into the trinitro-*o*-xylenes.

Experiment II.—Twenty-five grams of *o*-xylene were gradually added to 250 grams of fuming nitric acid, taking care to maintain the temperature at 22—25°, the whole allowed to stand one hour, then poured into water, and worked up in the usual manner. The residue left on evaporation of the ethereal solution solidified at once (41 grams), and, as it was proved not to contain any mononitro-*o*-xylene, it was directly treated for the separation of the dinitro-*o*-xylenes as already described, when it yielded 6·3 grams of 3 : 4-dinitro-*o*-xylene, 12·4 grams 4 : 6-dinitro-*o*-xylene, 6·6 grams of the mixture of 4 : 5-dinitro-*o*-xylene and 3 : 4-dinitro-*o*-xylene melting at 63—65°, and 7 grams of low melting, waxy solid.

Action of Nitric and Acetic Acids on o-*Xylene*

Twenty-five grams of *o*-xylene were added drop by drop to 150 grams of fuming nitric acid mixed with half its volume of glacial acetic acid, the temperature being kept between 20° and 25°. After treating a second quantity of *o*-xylene in a similar manner, the whole was poured into water and worked up exactly as described under the action of nitric acid on *o*-xylene, experiment I (compare page 215). There were obtained 52 grams of an oil which contained no dinitro-*o*-xylenes and yielded 11·5 grams of 4-nitro-*o*-xylene, 17·5 grams of 3-nitro-*o*-xylene, and 10 grams of a mixture of the two mononitro-*o*-xylenes, which, being too small an amount to fractionate further, was added to similar mixtures obtained in other experiments and the separation process repeated.

Action of Nitric and Sulphuric Acids on o-*Xylene.*

Fifty grams of fuming nitric acid and 100 grams of concentrated sulphuric acid were mixed and slowly added to 50 grams of *o*-xylene cooled in a freezing mixture, and the whole treated as described under the action of nitric acid on *o*-xylene (compare page 215), when 44 grams of mononitro-*o*-xylenes and 31 grams of dinitro-*o*-xylenes were obtained. From the 44 grams were isolated only 3 grams of pure 4-nitro-*o*-xylene, which was much less coloured than when prepared by the action of nitric acid alone on *o*-xylene, and 25 grams of 3-nitro-*o*-

xylene. The dinitro-*o*-xylenes consisted of the same mixture as isolated from the action of nitric acid alone on *o*-xylene.

The above experiment was repeated, using 30 grams of *o*-xylene and a mixture of 50 grams of fuming nitric acid and 100 grams of concentrated sulphuric acid, and adding the *o*-xylene to the nitrating mixture instead of vice versa. Under these slightly altered conditions, no mononitro-*o*-xylenes were formed, but a theoretical amount of dinitro-*o*-xylenes, which were separated as already detailed.

Summary.

Some thirty to forty experiments have been made on the nitration of *o*-xylene, using a variety of conditions, on the results of which the following general observations may be recorded :

1. Using fuming nitric acid alone and below −4° :

(*a*) Unchanged *o*-xylene is always recovered if less nitric acid is used than six times the weight of *o*-xylene.

(*b*) In all experiments, no matter how small an amount of nitric acid is employed, and even when unchanged *o*-xylene is recovered, dinitro-*o*-xylenes are formed.

(*c*) If the nitric acid is increased up to fifteen times the weight of *o*-xylene, the amount of dinitro-*o*-xylenes continually increases, but some mononitro-*o*-xylenes are always formed.

2. If *o*-xylene is nitrated with ten times its weight of fuming nitric acid at 22—25°, an almost theoretical yield of dinitro-*o*-xylenes is produced.

3. The above observations are only correct when *o*-xylene is added to nitric acid. If, on the other hand, nitric acid is added to *o*-xylene, a small amount of the latter is converted into mononitro-*o*-xylenes, together with a substance having the formula $C_{16}H_{17}O_2N$, which is at present being investigated.

4. Whereas with nitric acid alone about equal proportions of 3- and 4-nitro-*o*-xylenes are produced, with nitric and acetic acids the proportion of the former to the latter becomes 1·5 to 1. Moreover, with nitric and acetic acids no dinitro-*o*-xylenes are formed.

5. With nitric and sulphuric acids below 0° :

(*a*) When the nitrating mixture is added to *o*-xylene, the proportion of 3-nitro-*o*-xylene obtained is about eight times that of the 4-nitro-*o*-xylene.

(*b*) If, on the other hand, *o*-xylene is added to the mixture of acids, no mononitro-*o*-xylene, but a theoretical yield of dinitro-*o*-xylenes, is produced.

(*c*) Although giving rather a better yield of dinitro-*o*-xylenes than the action of nitric acid alone on *o*-xylene, this method is not to be recommended for their preparation, because a large proportion of 4 : 5-dinitro-*o*-xylene (m. p. 115°) is formed, and this crystallises from sulphuric acid together with 3 : 4-dinitro-*o*-xylene (m. p. 82°) as a constant melting mixture (63—65°), which can only be separated into its constituents by a tedious process of fractionation from large volumes of alcohol. As there is more 3 : 4-dinitro-*o*-xylene produced by the action of nitric acid alone, it follows that there must be less of the constant melting mixture, and consequently the 3 : 4-dinitro-*o*-xylene is more easily separated.

6. To ensure the above results, it is not advisable to nitrate more than 50 grams of *o*-xylene at one time.

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XXVIII.—*The Relation between the Chemical Constitution and Optical Properties of the Aromatic α- and γ-Diketones.*

By IDA SMEDLEY.

IN a previous paper (Trans., 1908, **93**, 372) the influence of the conjugation of benzenoid and ethenoid groups on the refractive power was discussed, and it was shown that the successive introduction of each unsaturated group into the molecule influences the whole series of unsaturated groups as long as they are all in conjunction. The investigation has now been extended to the unsaturated ketones, and the present communication contains an account of the behaviour of certain α- and γ-diketones. In a subsequent paper I hope to discuss the refractive power of the unsaturated ketones and of certain β-diketones.

EXPERIMENTAL.

Benzoylformaldehyde, $C_6H_5 \cdot CO \cdot CHO$.—This was prepared according to Müller and Pechmann's method (*Ber.*, 1887, **20**, 2904 ; 1889, **22**, 2557). The anhydrous aldehyde was purified by distillation under a pressure of 50 mm. (b. p. 120°). The deep yellow liquid was dissolved in chloroform, and its molecular refraction determined :

Strength of solution, 6·1313 per cent. M_α 36·99 ; M_β 38·66 ; $M_\beta - M_\alpha = 1 \cdot 67$. $\left(M = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{P}{d}\right)$.

Phenyl Methyl Diketone, $C_6H_5 \cdot CO \cdot CO \cdot CH_3$.—This substance was obtained from *iso*nitrosopropiophenone by heating it with dilute sulphuric acid and separating by steam distillation (Pechmann and Müller, *Ber.*, 1888, **21**, 2176). The dried diketone was twice redistilled under a pressure of 23 mm. (b. p. 123°); the refractive index of the pure substance was then determined for the *C*-line:

$$D^{20}_4 = 1\cdot10065;\ \mu_\alpha = 1\cdot52670;\ M_\alpha\ 41\cdot32.$$

In chloroform solution the following result was obtained:

Strength of solution, 3·0939 per cent. M_α 40·86; M_β 42·16; $M_\beta - M_\alpha = 1\cdot30$.

In preparing *iso*nitrosopropiophenone, it was found that the best yield (60—70 per cent.) was obtained by passing hydrogen chloride into a mixture of acetophenone and a 50 per cent. solution of ethyl nitrite in alcohol.

Dibenzoylethylene, $C_6H_5\cdot CO\cdot CH{:}CH\cdot CO\cdot C_6H_5$ (yellow form, m. p. 111°).—Molecular proportions of anhydrous benzoylformaldehyde and acetophenone were heated for one hour with an excess of acetic anhydride. The product was then poured into water, and, after some time, was washed with sodium carbonate solution, extracted with ether, and the ethereal solution dried. From this solution, yellow needles crystallised, which melted at 111° after recrystallisation from hot alcohol. Benzoylformaldehyde hydrate may be substituted for the anhydrous aldehyde in this condensation, but the yield is diminished. The refractive power was determined in chloroform solution.

Percentage strength of solution.	M_α.	M_β.	$M_\beta - M_\alpha$.
2·2926	74·00	77·92	3·92
4·0639	74·15	78·12	3·97
1·7982	73·74	77·96	4·22
Mean	73·96	78·00	4·04

Dibenzoylethylene (white form, m. p. 134°).—The yellow needles obtained above were dissolved in alcohol, the solution placed in a stoppered flask, and exposed to the influence of bright sunlight (Paal and Schulze, *Ber.*, 1902, **35**, 174); white needles, melting at 134°, gradually separated, thus showing the diminished solubility of the higher melting isomeride. The determination of the refractive power was made in chloroform solution.

Percentage strength of solution.	M_α.	M_β.	M_γ.	$M_\beta - M_\alpha$.
1·5627	71·72	75·54	76·34	3·82
3·1799	71·97	75·68	77·96 ?	3·71
2·1154	—	75·02	76·82	—
Mean	71·84	75·61	77·07 ?	3·76

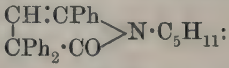
cis-*αβ-Dibenzoylstyrene*, $C_6H_5\cdot CO\cdot C(C_6H_5){:}CH\cdot CO\cdot C_6H_5$ (m. p.

129°).—The condensation of benzil and acetophenone was carried out according to the directions given by Japp and Klingemann (Trans., 1890, **57**, 662); the product, recrystallised from hot alcohol, consisted of pale yellow needles melting at 129°; the refractive power of this was determined in chloroform solution.

Percentage strength of solution.	M_α.	M_β.	$M_\beta - M_\alpha$.
4·4304	99·71	105·90	6·19
4·0263	99·49	105·55	6·06
6·0493	99·51	105·27	5·76
Mean	99·57	105·57	6·00

trans-*αβ-Dibenzoylstyrene* (m. p. 197—198°).—This compound was obtained in small quantities by Japp and Klingemann in the reactions between *cis*-dibenzoylstyrene and a primary alkylamine, a larger proportion being obtained when propylamine was used than with the amines of lower molecular weight. The *cis*-compound was therefore condensed with *iso*amylamine, an amine of still higher molecular weight, but on this occasion none of the *trans*-compound was detected in the mother liquors, the only product identified being amylpyrrolone, a homologue of the derivatives prepared by Japp.

Action of iso*Amylamine on* cis-*Dibenzoylstyrene.*—An alcoholic solution of *cis*-dibenzoylstyrene was heated with a slight excess of *iso*amylamine for one hour on a water-bath. The alcohol was distilled off, leaving an oily residue, from which after some days large, prismatic crystals were deposited melting at 66°. An analysis agreed with the formula for amylpyrrolone,



$\left.\begin{array}{l}\text{CH:CPh}\\ \text{CPh}_2\cdot\text{CO}\end{array}\right>\text{N}\cdot\text{C}_5\text{H}_{11}$:

0·1344 gave 0·4171 CO_2 and 0·0927 H_2O. C = 84·67; H = 7·67.

$C_{27}H_{27}ON$ requires C = 85·04; H = 7·80 per cent.

Action of Aromatic Bases.—Prolonged boiling in aniline and in quinoline solutions respectively does not appear to convert the *cis*- into the *trans*-form; almost the whole of the original substance was recovered unchanged in each case.

Small quantities of the *trans*-compound were detected in the mother liquors from which the *cis*-form of dibenzoylstyrene had been crystallised. If the calculated amount of alcoholic potash is added to a boiling solution of benzil and acetophenone in alcohol and the mixture heated on a water-bath for half an hour, the amount of the *trans*-compound in solution appears to be slightly increased.

s-*Dibenzoylstilbenes.*—A repetition of Zinin's work on these substances confirmed the observation made by Japp that the melting point of the *cis*-compound by repeated recrystallisation is not raised above 211° (Japp and Klingemann, *loc. cit.*). Zinin gives 220° as the melting point.

The measurements of the refractive power were made in chloroform solution. The comparative insolubility of the *trans*-compound renders the value obtained for its refraction less trustworthy than that of the *cis*-form.

	Percentage strength of solution.	M_a.
cis-Diphenylstilbene	1·5651	122·49
	1·9959	123·21
Mean....................	—	122·76
trans-Diphenylstilbene	0·6221	122·56
	0·6072	124·87
Mean....................	—	123·71

THEORETICAL.

(1) *The a-Diketones.*

Armstrong and Robertson (Trans., 1905, **87**, 1275) first pointed out that contiguous carbonyl groups in open-chain compounds appear to exert no special influence on refractive power, but that an exaltation is produced by the same grouping in benzenoid compounds. This observation seems not to have been noticed by Brühl (*Ber.*, 1907, **40**, 1153), who wrote subsequently that exaltation in refractive power is never produced by the conjugation of two carbonyl groups; the cases he quotes are, however, taken only from the aliphatic series.

Amongst the α-diketones already examined, the molecular refraction of benzil alone is markedly greater than the calculated value; the determination of the refractive power of the monophenyldicarbonyl compounds, such as phenyl methyl diketone, $C_6H_5{\cdot}CO{\cdot}CO{\cdot}CH_3$, and benzoylformaldehyde, $C_6H_5{\cdot}CO{\cdot}CHO$, shows that the exaltation in the refractive power of benzil is connected with the presence of both phenyl groups. In the table on page 222 the values actually observed are compared with those calculated for the refractive power of these compounds.

It is obvious that the difference between the calculated and observed values in benzil is very much greater than the corresponding difference in the aliphatic and monophenyl derivatives. That there is a slight exaltation in the refractive power of the monophenyl derivatives is more evident if the molecular refractions of the similarly constituted mono- and di-ketones are compared, for the slightly larger influence of the carbonyl group in benzaldehyde as compared with that in acetophenone masks the exaltation when the above method of calculation is employed.

	$M_\alpha\left(\frac{\mu_{\alpha}^2-1}{\mu_{\alpha}^2+2}\cdot\frac{M}{d}\right)$		
	Observed.	Calculated.*	Difference.
Diacetyl	...	$CH_3{\cdot}CHO = 11{\cdot}50$	
		$CH_3{\cdot}CHO = 11{\cdot}50$	
		23·00	
		$-H_2 =$ 2·206	
$CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$	20·84 (Brühl)	20·79	+0·05
Phenyl methyl diketone.	...	$C_6H_5{\cdot}CHO = 31{\cdot}77$	
		$CH_3{\cdot}CHO = 11{\cdot}50$	
		43·27	
		$-H_2 =$ 2·206	
$C_6H_5{\cdot}CO{\cdot}CO{\cdot}CH_3$	41·32 (see page 218)	41·06	+0·26
Benzoyl ormaldehyde.	...	$C_6H_5{\cdot}CHO = 31{\cdot}77$	
		$CH_3{\cdot}CHO = 11{\cdot}50$	
		43·27	
		$-CH_4 =$ 6·61	
$C_6H_5{\cdot}CO{\cdot}CHO$	36·99 (see page 218)	36·66	+0·33
Benzil	...	$C_6H_5CHO = 31{\cdot}77$	
		$C_6H_5CHO = 31{\cdot}77$	
		63·54	
		$-H_2 =$ 2·206	
$C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$......	63·48 (Anderlini)	61·33	+2·14

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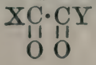
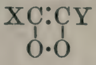
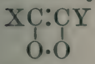
* Calculations using the atomic refractions of the elements given by Brühl do not allow for the exaltation produced by the conjugation of a phenyl with a carbonyl group.

The effect of phenyl on the value of the carbonyl group is well shown by the following table:

	M_α (observed).		M_α (observed).		M_α (observed).
Diacetyl, $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$	20·8	Phenylmethyldiketone, $C_6C_5{\cdot}CO{\cdot}CO{\cdot}CH_3$	41·32	Benzil, $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$	63·48
Acetone, $CH_3{\cdot}CO{\cdot}CH_3$ ...	16·05	Acetophenone, $C_6H_5{\cdot}CO{\cdot}CH_3$	36·00	Benzophenone, $C_6H_5{\cdot}CO{\cdot}C_6H_5$ ...	56·20
	CO = 4·75		CO = 5·32		CO = 7·28
		Benzoylformaldehyde, $C_6H_5{\cdot}CO{\cdot}CHO$	36·99		
		Benzaldehyde, $C_6H_5{\cdot}CHO$ ...	31·77		
			CO = 5·22		

The α-diketones are distinguished by their intense yellow colour and their chemical reactivity, these properties being least apparent in benzil. The absorption spectra of diacetyl and benzil were examined by Baly and Stewart (Trans., 1906, **89**, 502), who showed that in benzil the absorption band characteristic of diacetyl is present, although it is much less marked. The same authors attribute the existence of the absorption band to an oscillation of the molecule between the two phases represented by the formulæ :

(*a*)  $\begin{array}{c}XC\cdot CY\\ \| \quad \| \\ O \quad O\end{array}$ and (*b*)  $\begin{array}{c}XC\colon CY\\ | \quad | \\ O\cdot O\end{array}$.

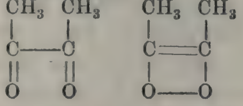
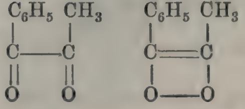
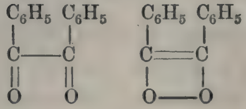
The chief difficulty in accepting this explanation lies in the necessary assumption that a compound represented by the formula  $\begin{array}{c}XC\colon CY\\ | \quad | \\ O\cdot O\end{array}$ exists only as an unstable phase ; but the yellow colour of the simplest member of the series, glyoxal (CHO·CHO), in contrast to the absence of colour observed in simple ketonic and ethenoid compounds, appears as very strong evidence of the mutual influence of the oxygen atoms.

It would follow as a deduction from Baly and Stewart's hypothesis that if such an oscillation is taking place at any one moment a certain proportion of the molecules would be in the state represented by the phase (*b*) ; in certain cases where X and Y are unsaturated groups, such a change in structure would probably be accompanied by an increase in the refractive power, and this might furnish a means of quantitatively investigating the change produced.

An exaltation in the refractive power of the α-diketones might be expected either when a certain number of molecules were present in each of the above phases (*a*) and (*b*), or when the molecules were in some intermediate state ; in the latter case the mutual attraction of the two oxygen atoms may be regarded as diminishing the carbon-oxygen attraction, and occasioning an increased attraction between the two carbon atoms.

It is unlikely that the linking together of the two oxygen atoms would tend to augment the refraction, since in all cases yet observed the closing of a saturated heterocyclic ring does not affect the refractive power (Brühl, *Ber.*, 1879, **12**, 2146 ; 1891, **24**, 657 ; *Annalen*, 1880, **203**, 43 ; Eykman, *Ber.*, 1892, **25**, 3071), and the formation of an unsaturated heterocyclic ring without exocyclic conjugation is invariably accompanied by a diminution in refractive power (Brühl, *Ber.*, 1907, **40**, 1157).

A comparison of the molecular refractions calculated for the two phases (*a*) and (*b*) with the values actually observed, affords evidence which is in harmony with the conclusion arrived at by Baly and Stewart (*loc. cit.*).

	Mα (calculated for diketo-phase).	Mα (calculated for peroxide phase).	Mα (observed).
Diacetyl ……		$CH_2{:}CH_2$ = 10·77 $2CH_2$ = 9·14 $2O'$ = 3·00 22·91 $-2H$ = 2·21	
	20·79 (see p. 222)	20·70	20·84
Phenyl methyl diketone …		$C_6H_5{\cdot}CH{:}CH_2$ = 35·98 $2O'$ = 3·00 CH_2 = 4·57 43·55 $-2H$ = 2·21	
	41·06 (see p. 222)	41·34	41·32
Benzil ………		$C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$ = 65·65 $2O'$ = 3·00 68·65 $-2H$ = 2·21	
	61·33 (see p. 222)	66·44	63·48

From the above table it will be seen that, in diacetyl, the effect produced by the two carbonyl groups would be about equal to that of an ethenoid group combined with two singly-linked oxygen atoms; determination of the refractive power will not therefore aid in distinguishing between the two phases.

The displacement of one methyl group in diacetyl by a phenyl group leads to a difference of 0·3 between the molecular refractions calculated for the two possible phases; the value observed agrees closely with the number deduced for the peroxide formula, but the calculated difference is so small that no trustworthy conclusion can be drawn from it.

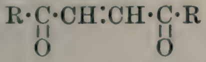
When both methyl groups are displaced by phenyl groups, it is shown that the change from the diketonic to the ethenoid structure would probably produce an increment in refractive power of about 5 units; the existence of a number of the molecules in the phase (*b*) would therefore furnish an explanation of the abnormally high molecular refraction of benzil, the increment actually observed being 2·1 units above that calculated for the diketonic form, and corresponding with the existence of approximately 40 per cent. of the ethenoid phase.

The influence of the phenyl group in diminishing the intensity of colour in the aromatic diketones, when compared with the corresponding hydrogen or methyl derivatives, is apparent, not only here, but also in the phenyl derivatives of the dibenzoylethylenes, to which reference will be made later. If the explanation of Baly and Stewart be accepted, we may regard the tendency to oscillation as diminished by the weighting of the molecule, or possibly by the attraction exercised on the carbonyl group by the residual affinity of the phenyl group (compare Armstrong and Robertson, *loc. cit.*).

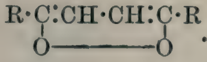
(2) *The Unsaturated γ-Diketones.*

It is unlikely that the structure $XCO\cdot CH_2\cdot COY$ would permit of a rearrangement of the oxygen valencies similar to that figured on page 223; and in accordance with this view we find that the β-diketones are white, and that their absorption spectra do not show the band in the visible region of the spectrum characteristic of the α-diketones, but contain only those bands in the ultra-violet which, according to Baly (Trans., 1904, **85**, 1029), are typical of compounds capable of existing in both enolic and ketonic forms.

If, however, an ethenoid group be substituted for the $\cdot CH_2\cdot$, a rearrangement similar to that figured in the case of the α-diketones on p. 223 becomes possible.

(*a*) 

$R\cdot\underset{\underset{O}{\|}}{C}\cdot CH{:}CH\cdot\underset{\underset{O}{\|}}{C}\cdot R$

(*b*) 

$R\cdot\underset{\underset{O}{|}}{C}{:}CH\cdot CH{:}\underset{\underset{O}{|}}{C}\cdot R$.

Both *cis*- and *trans*-modifications of the phase (*a*) are possible, and of these the oxygen atoms in the *cis*-modification might be expected to exhibit most strongly mutual attraction; on this assumption it is conceivable that a yellow *cis*-form and a colourless *trans*-form of these diketones might occur. The refractive power of the yellow *cis*-form should then be appreciably higher than that of the colourless *trans*-form.

If the arrangement in space of the atoms constituting the α-, β-, and γ-diketones respectively is considered, it is evident that in the α- and γ-positions the oxygen atoms approach more nearly to each other than in the β-position, and are therefore more likely to be within the region of mutual influence. Since, however, the saturated γ-diketones (for example, dibenzoylethane) are colourless, the position in space of the oxygen atoms is not in itself sufficient to condition colour. In order that the substance may be coloured, it appears to be essential that the carbonyl groups are connected by an ethenoid group.

(*a*) *The* cis- *and* trans-s-*Dibenzoylethylenes,*
$C_6H_5\cdot CO\cdot CH{:}CH\cdot CO\cdot C_6H_5$.

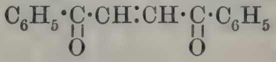
A mixture of the stereoisomeric *s*-dibenzoylethylenes was obtained by Paal and Schulze (*Ber.*, 1900, **33**, 3784; 1902, **35**, 168) on heating dibenzoylmalic acid. The two compounds consist of (1) yellow needles melting at 111°, passing, when the alcoholic solution is exposed to bright sunlight, into (2), white needles melting at 134°. The colourless modification reacts much more readily with hydrazine hydrate to form a pyridazine ring, and the *cis*-configuration was therefore ascribed to it by Paal and Schulze as being the most favourable position for the ring formation.

In investigating this matter I find that the yellow modification is more conveniently prepared by condensing benzoylformaldehyde with acetophenone in the presence of acetic anhydride; alkaline condensing agents must be avoided, owing to the extreme readiness with which benzoylformaldehyde is converted by them into mandelic acid.

The higher melting point of the white isomeride, and the fact that it is the more sparingly soluble form, appear to me to indicate that the white and not the yellow isomeride should be represented as the *trans*-configuration.

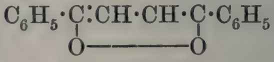
The evidence furnished by the α-diketones shows that the mutual influence of two carbonyl oxygen atoms produces absorption in the visible region of the spectrum; in the γ-diketones, this mutual influence of the oxygen atoms will be more likely to be exerted in the *cis*-modification, where the oxygen atoms approach more nearly to each other. The occurrence of a yellow *cis*-modification and a colourless *trans*-form would therefore agree better with the view already advanced with regard to the relations between the colour and constitution of the α-diketones. Further, if the colour of the yellow modification be due to an oscillation similar to that assumed to be taking place in the α-diketones, its molecular refraction should lie between the values calculated for the two phases:

(*a*)



$C_6H_5\cdot\underset{\underset{O}{\|}}{C}\cdot CH{:}CH\cdot\underset{\underset{O}{\|}}{C}\cdot C_6H_5$

and (*b*)

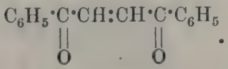


$C_6H_5\cdot\underset{\underset{O}{|}}{C}{:}CH\cdot CH\cdot\underset{\underset{O}{|}}{C}\cdot C_6H_5$

whilst the value for the *trans*-modification should agree with that calculated for the formula (*a*).

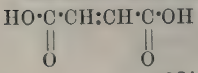
The calculation of the molecular refractions for these two phases may be made in the following manner:

(*a*)



$C_6H_5\cdot\underset{\underset{O}{\|}}{C}\cdot CH{:}CH\cdot\underset{\underset{O}{\|}}{C}\cdot C_6H_5$.

M_α-Maleic acid (Kannonikoff).



$HO\cdot\underset{\underset{O}{\|}}{C}\cdot CH{:}CH\cdot\underset{\underset{O}{\|}}{C}\cdot OH$ = 23·94

$-2O'$ = 3·00 ——— 20·94

Displacement of H by C_6H_5 when joined to a CO group:

$C_6H_5\cdot CO\cdot CH_3$ = 36·00

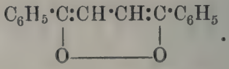
$H\cdot CO\cdot CH_3$ = 11·05

2 × 24·95 = 49·90

———

70·84

(*b*)



$C_6H_5\cdot\underset{\underset{O}{|}}{C}{:}CH\cdot CH{:}\underset{\underset{O}{|}}{C}\cdot C_6H_5$.

M_α-Diphenylbutadiene (Trans., 1908, **93**, 376).

$C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot C_6H_5$ = 82·90

$-2H$ = 2·21

———

80·69

$2O'$ = 3·00

———

83·69

83·69

The values actually observed are:

	M_a.
Yellow form (melting point 111°)	74·0
White ,, (,, ,, 134°)	71·8

The molecular refraction found for the white form (71·8) is slightly higher than that calculated for the diketonic form (70·8); this would be expected, since a phenyl group joined to a $\cdot CO \cdot CH \colon CH \cdot CO \cdot$ group would probably produce a slightly greater effect than a phenyl group joined to a $\cdot CO \cdot CH_3$ group, the number adopted in the calculation. The refractions are sufficiently in agreement, however, to justify the assumption that the diketonic structure should be assigned to the white form.

The higher value (74·0) obtained for the yellow modification may be regarded as consistent with the view that in this form a small percentage of the compound may exist in an isomeric phase, having a butadiene structure, and the value 74·0 would correspond with the presence of about 18 per cent. of this form. It has already been pointed out that the figures obtained for benzil indicate the existence of about 40 per cent. of the ethenoid phase.

It follows, therefore, that the study of the refractive power of these compounds supports the view that the yellow modification is to be regarded as the *cis*-form.

The diminished reactivity of the yellow *cis*-form when treated with hydrazine hydrate may be due to the mutual influence of the two carbonyl oxygen atoms. The comparative inertness of the carbonyl oxygen in the carboxyl group furnishes an instance of the marked effect of a second oxygen atom attached to the same carbon atom; in *cis*-dibenzoylethylene, it is suggested that an influence similar in character but much less strongly marked may be at work.

(*b*) *The Phenyl Derivatives of* s-*Dibenzoylethylene*: (i) cis- *and* trans-*Dibenzoylstyrenes*, $C_6H_5 \cdot CO \cdot CH \colon C(C_6H_5) \cdot CO \cdot C_6H_5$.

The *cis*- and *trans*-forms of dibenzoylstyrene were obtained by Japp and Klingemann (Trans., 1890, **57**, 662). The *cis*-form, consisting of pale yellow needles melting at 129°, is the product of the condensation of benzil and acetophenone with alkali. The *trans*-form, colourless and of higher melting point (197—198°), occurs in small quantities as a by-product when the *cis*-isomeride is condensed with a primary alkylamine, and very small quantities are also formed when the *cis*-modification is heated.

If Japp's conclusions be accepted, the analogy between the coloured and colourless modifications of dibenzoylethylene and of its monophenyl derivative confirms the conclusion that the yellow dibenzoylethylene is to be regarded as the *cis*-modification.

The determination of the molecular refraction of the *cis*-form gave the value 99·6. Sufficient of the *trans*-modification was not obtained to enable a trustworthy determination of its refractive power to be made ; experiments made with the object of increasing the yield of the *trans*-compound have not led to satisfactory results.

(ii) cis- *and* trans-*Dibenzoylstilbenes*,

$$C_6H_5\cdot CO\cdot C(C_6H_5)\colon C(C_6H_5)\cdot CO\cdot C_6H_5.$$

These substances, originally prepared by Zinin, and named by him acicular and octahedral oxylepidenes, were subsequently identified by Japp and Klingemann (*loc. cit.*) as the *cis*- and *trans*-modifications of dibenzoylstilbene.

The *cis*-modification consists of very pale yellow needles, melting at 211°, the *trans*-form of needles, which are much less sparingly soluble and melt at 232°. The latter are also pale yellow, and by repeated crystallisation I have not been able to obtain a colourless specimen.

The refractive power of both forms was measured in chloroform solution ; the values found were for the *cis*-form, 122·8, and for the *trans*-form, 123·7. Owing to the insolubility of the *trans*-form, the determination of its refractive power is less trustworthy than that of the *cis*-form. No such difference in the values obtained for the two forms as that described (p. 227) in the case of the two dibenzoylethylenes was detected. If such a difference exists, it is smaller and of an order comparable with the degree of experimental error.

In the following table, a comparison of the properties of these substances is shown :

	cis-Form.			*trans*-Form.		
	Colour.	M. p.	M_α.	Colour.	M. p.	M_α.
Dibenzoylethylene, COPh·CH:CH·COPh ...	Yellow	111°	74·0	White	134°	71·8
Dibenzoylstyrene, COPh·CPh:CH·COPh ..	Pale yellow	129°	99·6	White	197°	—
Dibenzoylstilbene, COPh·CPh:CPh·COPh..	Very pale yellow	211°	122·8	Very pale yellow	232°	123·7

These compounds furnish an interesting example of a case where the introduction of phenyl groups, not only does not intensify, but actually diminishes the colour. In conjunction with Miss M. B. Thomas, I am at present investigating the absorption spectra of these substances, and propose to extend this investigation to other substances containing the grouping $\cdot CO\cdot CH\colon CH\cdot CO\cdot$. The diminution in colour is, however, obvious to the eye; on the hypothesis discussed above, this might be assumed to be due to the presence of the phenyl groups attached to the ethenoid carbon atoms diminishing the mutual influence of the oxygen atoms, a smaller percentage of the compound existing in the butadiene phase. The attraction between the two oxygen atoms is diminished by the introduction of one phenyl group, and, when a second phenyl group is introduced, becomes so small as to be no longer detected when the refractive power is examined.

This conclusion is supported by a comparison of the increments in the refractions produced by the substitution of successive phenyl groups; the displacement of an ethylenic hydrogen in dibenzoylethylene by one phenyl group produces an increment of 25·6 units; the increment when the second phenyl group is introduced is, however, only 23·2 units. This is confirmatory evidence that the refractive value of the *cis*-form of the diphenyl compound is now no longer exalted above that of the *trans*.

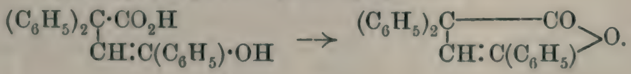
The influence of the phenyl groups is probably similar to that noticed above in discussing the colour of benzil. The accumulation of phenyl groups in the molecule complicates the question, since a sufficient number of conjugated unsaturated hydrocarbon groups are themselves able to produce absorption in the visible region of the spectrum, for example, in diphenylhexatriene (Smedley, Trans., 1907, **93**, 372).

The resemblance between the *a*-diketones and the symmetrical diacylethylenes is not confined to their physical properties; it is also evident from a consideration of their chemical behaviour. Benzil and the phenyl derivatives of dibenzoylethylene both furnish remarkable instances of the wandering of a phenyl group; the transformation of benzil into benzilic acid on treatment with alkali is entirely analogous to the reactions described by Japp and Klingemann (*loc. cit.*), which occur when dibenzoylstyrene is heated, and when it is treated with a primary alkyl amine:

(*a*) $C_6H_5\cdot CO\cdot CO\cdot C_6H_5 + H_2O = (C_6H_5)_2C(OH)\cdot CO_2H.$

(*b*) $C_6H_5\cdot CO\cdot C(C_6H_5){:}CH\cdot CO\cdot C_6H_5 + H_2O =$

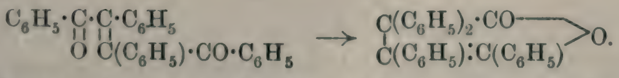
$$(C_6H_5)_2C(CO_2H)\cdot CH_2\cdot CO\cdot C_6H_5 \longrightarrow$$



$$\begin{array}{l}(C_6H_5)_2C\cdot CO_2H\\ \qquad\quad CH{:}C(C_6H_5)\cdot OH\end{array} \longrightarrow \begin{array}{l}(C_6H_5)_2C\text{———————}CO\\ \qquad\quad CH{:}\,C(C_6H_5)\end{array}\!\!>O.$$

Similarly:

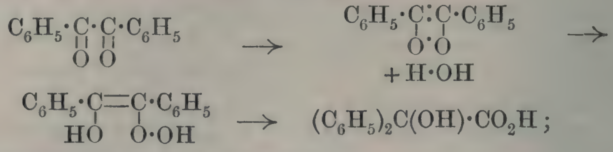
(*c*)



$$\begin{array}{l}C_6H_5\cdot \underset{\|}{C}\cdot \underset{\|}{C}\cdot C_6H_5\\ \qquad\quad O\;\; C(C_6H_5)\cdot CO\cdot C_6H_5\end{array} \longrightarrow \begin{array}{l}C(C_6H_5)_2\cdot CO\text{———}\\ C(C_6H_5){:}C(C_6H_5)\end{array}\!\!>O.$$

It is difficult to give any explanation of these reactions with the usual formulæ, but the interpretation is simpler if it be assumed that the ketones react in the peroxide form as follows:

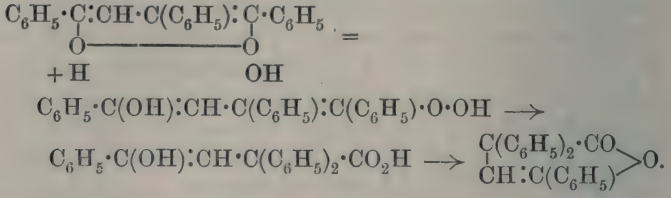
(*a*)



$$C_6H_5\cdot\underset{O}{\underset{\|}{C}}\cdot\underset{O}{\underset{\|}{C}}\cdot C_6H_5 \rightarrow \underset{+H\cdot OH}{C_6H_5\cdot\underset{O\cdot}{\underset{|}{C}}:\underset{O}{\underset{|}{C}}\cdot C_6H_5} \rightarrow$$

$$C_6H_5\cdot\underset{HO}{\underset{|}{C}}=\underset{O\cdot OH}{\underset{|}{C}}\cdot C_6H_5 \rightarrow (C_6H_5)_2C(OH)\cdot CO_2H;$$

(*b*)



$$\underset{+H\qquad\qquad\qquad OH}{C_6H_5\cdot\underset{O}{\underset{|}{C}}:CH\cdot C(C_6H_5):\underset{O}{\underset{|}{C}}\cdot C_6H_5} =$$

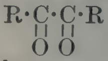
$$C_6H_5\cdot C(OH):CH\cdot C(C_6H_5):C(C_6H_5)\cdot O\cdot OH \rightarrow$$

$$C_6H_5\cdot C(OH):CH\cdot C(C_6H_5)_2\cdot CO_2H \rightarrow \begin{matrix}C(C_6H_5)_2\cdot CO\\ CH:C(C_6H_5)\end{matrix}\!\!>O.$$

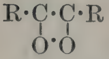
This explanation has the advantage of showing why only one phenyl group of the diphenyl derivative suffers rearrangement.

Conclusions.

(1) The refractive power of benzil appears to be intermediate between the values calculated for the two phases,



$\underset{O}{\underset{\|}{R\cdot C}}\cdot\underset{O}{\underset{\|}{C}}\cdot R$ and



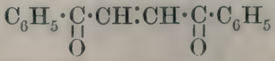
$R\cdot\underset{O\cdot}{\underset{|}{C}}\cdot\underset{O}{\underset{|}{C}}\cdot R$, and is in accordance therefore with Baly and Stewart's view that an oscillation between these two forms is taking place.

(2) The refractions calculated for the two phases in aliphatic compounds do not differ sufficiently to enable one to decide between the two possibilities.

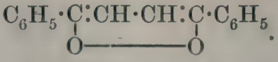
(3) In the series of unsaturated γ-diketones, the compound having the lower melting point, greater solubility, and yellow colour is the *cis*-modification, and the yellow modification of dibenzoylethylene (described by Paal and Schulze as the *trans*-form) should therefore be considered as the *cis*-configuration.

(4) There is a marked difference between the molecular refractions of the *cis*- and *trans*-dibenzoylethylenes.

(5) The molecular refraction of *trans*-dibenzoylethylene agrees with that calculated for the diketonic compound, whereas that observed for the *cis*-compound is higher, and is intermediate between the refractions calculated for the two phases:



$C_6H_5\cdot\underset{O}{\underset{\|}{C}}\cdot CH:CH\cdot\underset{O}{\underset{\|}{C}}\cdot C_6H_5$ and



$$C_6H_5\cdot\underset{O}{\underset{|}{C}}:CH\cdot CH:\underset{O}{\underset{|}{C}}\cdot C_6H_5.$$

(6) The *cis*-unsaturated γ-diketones show many resemblances to the α-diketones.

(7) The substitution of two phenyl groups for the alkyl groups in the aliphatic α-diketones, or for the ethylenic hydrogen in the diacylethylenes, is accompanied by a diminution in colour, attributable to the mutual influence of the phenyl and oxygen, whereby the residual affinity of the two carbonyl oxygen atoms is diminished.

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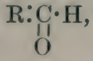
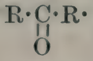
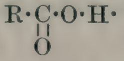
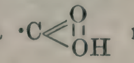
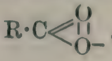
XXIX.—*Note on the Constitution of the Carboxyl Group.*

By IDA SMEDLEY.

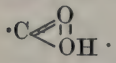
COMPOUNDS usually represented as containing two adjacent carbonyl radicles may be divided into two classes, namely, one comprising the intensely yellow diketones and glyoxal (Harries and Jemme, *Ber.*, 1907, **40**, 165), the other the colourless oxalic acid with its esters, amide, and chloride. This distinction is not confined to the physical properties of these substances, but is equally evident when their chemical behaviour is considered; on the one hand we have in the ketones and aldehydes a class of compounds readily reducible and reacting easily with such reagents as phenylhydrazine, hydroxylamine, and semicarbazide; on the other hand the carboxylic acids are substances which can be reduced only with the greatest difficulty and are inert towards the usual reagents for aldehydes and ketones.

The formulæ  $R{:}\underset{\underset{O}{\|}}{C}\cdot H$,  $R\cdot\underset{\underset{O}{\|}}{C}\cdot R\cdot$ and  $R\cdot\underset{\underset{O}{\|}}{C}\cdot O\cdot H\cdot$ usually assigned to aldehydes, ketones and carboxylic acids, do not offer an adequate explanation of these great differences in behaviour, and it seems to the author that the formula  $\cdot C\!<\!\begin{array}{l}O\\ \|\\ OH\end{array}$ may probably be a more correct expression for the carboxyl group. The residual affinity of the carbonyl oxygen, which is exhibited so markedly in the formation of the oxonium compounds, is here represented as being satisfied by the hydroxylic oxygen, and the active carbonyl group is no longer figured as present. It may be pointed out that the close connexion of the two oxygen atoms with each other and with the carbon atom accounts well for the ease with which carbon dioxide is eliminated from the carboxylic acids.

Further, the marked acidity of the carboxylic hydrogen is explained by its attachment to the group  $R\cdot C\!<\!\begin{array}{l}O\\ \|\\ O-\end{array}$. In a discussion on the constitution of the benzoyl peroxides, Baeyer and Villiger (*Ber.*, 1900, **33**, 1569) point out that the organic acids do not owe their acid properties to the piling up of the oxygen atoms, but to the "unmittelbare Verbindung" of the carbonyl and hydroxyl groups. They instance the fact that the displacement of a hydrogen atom from water by an acetyl group produces an acid, whereas the substitution of acetyl for a hydrogen of hydrogen peroxide does not lead to the acquisition of acid properties.

Brühl (*Ber.*, 1907, **40**, 896) has also pointed out that the exaltation of refractive power in aromatic aldehydes and ketones is greater than in the corresponding acids and esters. He attributes this to the greater degree of unsaturation in the former class of compounds, and suggests that a partial neutralisation of the supplementary affinities of the two oxygen atoms occurs, which may be compared to the "neutral conjugation of the ethenoid linkings in the benzene ring."

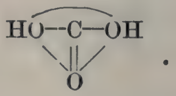
The slight difference in the refraction value which exists between the carbonyl group in the aldehyde and in the acid would agree well with the representation of the carboxyl group by the formula



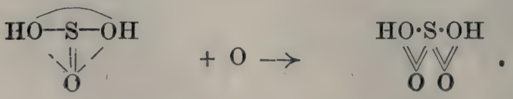
$\cdot\mathrm{C}\begin{matrix}\mathrm{O}\\ \mathrm{OH}\end{matrix}\cdot$

Although the reactions depending on the acid character of the hydrogen are well marked, many of the reactions characteristic of the hydroxyl group are absent in carboxylic acids; thus the hydroxyl is not readily replaced by chlorine on treatment with hydrochloric acid.

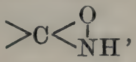
It is possible that the instability of carbonic acid may be connected with the symmetrical arrangement of the carbonyl oxygen between two hydroxyl groups, thus:



In this connexion it is perhaps permissible to contrast the relative stability of sulphurous and sulphuric acids and to suggest that a similar influence may be at work.



In the derivatives of the carboxylic acids, the substitution for the hydroxyl group of an element or group of elements possessing residual affinity which can similarly attract the carbonyl oxygen probably leads to no change in structure. If the formula $\mathrm{R{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{OH}}$ be accepted for the fatty acids, the representation of the amides by the formula $\mathrm{R{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{NH{\cdot}H{\cdot}}}$ would be in keeping with the known similarity of the amino- and hydroxyl groups. This structure would be in harmony with the evidence obtained from a study of the refractive power of the acid amides, the value of the atomic refraction of the nitrogen atom in an acid amide being slightly less than its value in an amine (Brühl, *Ber.*, 1907, **40**, 1157). The displacement of the hydrogen by metals and the formation of two classes of metallic derivatives in which the metal is attached to oxygen and nitrogen respectively (Titherley, Trans., 1901, **79**, 410) might be conveniently represented by the formulæ $\mathrm{R{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{NH{\cdot}H}}$ and $\mathrm{R{\cdot}C}{\lessdot}^{\mathrm{OH}}_{\mathrm{N{\cdot}H{\cdot}}}$. It will be remembered that a C·O·N· ring of a different type,



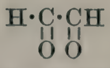
$$>\mathrm{C}<^{\mathrm{O}}_{\mathrm{NH}},$$

has been suggested by M. A. Whiteley (Trans., 1903, **83**, 30) as the configuration of the colourless forms of certain oximes.

When the structure of the acid chlorides is considered, the evidence appears somewhat conflicting. Staudinger (*Ber.*, 1908, **41**, 3558) has recently confirmed the earlier observation of Fauconnier (*Compt. rend.*, 1902, **114**, 122) that oxalyl chloride, $\begin{array}{c}\mathrm{COCl}\\ |\\ \mathrm{COCl}\end{array}$, is a colourless, fuming liquid. This would lead to the expression $\mathrm{R{\cdot}C}{\lessdot}^{\mathrm{O}}_{\mathrm{Cl}}$ for the acid chlorides; and the great reactivity of the atom might well be due to its close association with the negative oxygen atom.

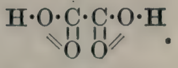
On the other hand, according to Brühl (*loc. cit.*), the refractive value of the carbonyl group in the acid chlorides more closely resembles that of the same group in the aldehydes and ketones.

Glyoxal and oxalic acid would on this hypothesis be represented as follows:



$$\begin{array}{c}\mathrm{H{\cdot}C{\cdot}CH}\\ \|\ \ \|\\ \mathrm{O\ \ O}\end{array}$$

Glyoxal (yellow).

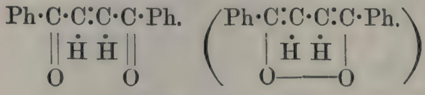


$$\begin{array}{c}\mathrm{H{\cdot}O{\cdot}C{\cdot}C{\cdot}O{\cdot}H}\\ \diagdown\|\ \ \|\diagup\\ \mathrm{O\ \ O}\end{array}.$$

Oxalic acid (white).

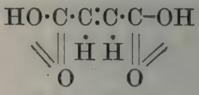
It will be seen that in glyoxal the residual affinity of the two oxygen atoms may conceivably bring about a change into the tautomeric modification $\begin{array}{c}\mathrm{HC{:}CH}\\ |\ \ |\\ \mathrm{O{\cdot}O}\end{array}$; in oxalic acid, however, the mutual attraction of the two oxygen atoms linked to the same carbon atom is assumed to be sufficient to overcome the attraction of the oxygen atoms bound to adjacent carbon atoms, or at any rate so far to diminish the latter that it has no longer an appreciable effect on the optical properties. Hence in accordance with Baly and Stewart's hypothesis (*loc. cit.*), glyoxal is yellow, whilst oxalic acid is white.

The following formulæ would then be assigned to *cis*-dibenzoylethylene and to maleic acid :



$$Ph\cdot\underset{O}{\underset{\|}{C}}\cdot\underset{\dot{H}}{C}\colon\underset{\dot{H}}{C}\cdot\underset{O}{\underset{\|}{C}}\cdot Ph. \qquad \left(Ph\cdot C\colon\underset{\dot{H}}{C}\cdot\underset{\dot{H}}{C}\colon C\cdot Ph.\right)$$

cis-Dibenzoylethylene.



$$HO\cdot\underset{O}{\underset{\|}{C}}\cdot\underset{\dot{H}}{C}\colon\underset{\dot{H}}{C}\cdot\underset{O}{\underset{\|}{C}}-OH$$

Maleic acid.

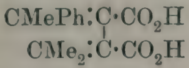
These formulæ afford an explanation of the fact that no difference in refractive power and no distinction in colour has been observed between the *cis*- and *trans*-forms of the ethylenedicarboxylic acids such as those which distinguish the *cis*- and *trans*-dibenzoylethylenes (compare p. 228).

The refractive powers of some derivatives of the ethylenecarboxylic acids are shown in the following table :

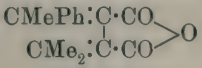
	M_α (observed).	M_α calculated from atomic refractions.	Difference : Effect due to conjugation 2CO groups with an ethenoid group.	Difference between *cis*- and *trans*-forms.	Observer.
Ethyl maleate......	42·23	41·85	0·38	—	Knops (*Annalen*, 1888, **248**, 175).
Ethyl fumarate ...	42·90	,,	1·05	+0·67	Knops.
Propyl maleate ...	51·34	50·79	0·59	—	,,
,, fumarate ...	51·70	,,	0·95	+0·36	,,
Citraconic acid ...	28·87	27·93	0·94	—	Kannonikoff (*J. pr. Chem.*, 1885, [ii], **31**, 320).
Mesaconic acid......	28·83	,,	0·90	−0·04	Kannonikoff.
Methyl citraconate	37·84	37·28	0·56	—	Knops (*loc. cit.*)
,, mesaconate	38·03	,,	0·75	+0·19	,,
Ethyl citraconate..	46·48	46·42	0·06 ?	—	,,
,, mesaconate..	47·39	,,	0·97	+0·91	,,

The differences observed between the molecular refractions of the corresponding *cis*- and *trans*-compounds are so small that they do not allow inferences as to constitution to be drawn with safety. It is interesting, however, to observe that the values obtained on examining the magnetic rotations of these substances are somewhat higher for the *trans*- than for the *cis*-isomerides (Perkin, Trans., 1896, **69**, 1145).

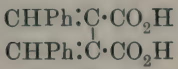
Confirmatory evidence of the influence of the hydroxyl oxygen on the carbonyl oxygen is afforded by a comparison of the fulgenic acids and their fulgides. It has been pointed out by Stobbe (*Annalen*, 1906, **349**, 367) that as a general rule the presence of oxygen in a ring tends to diminish colour. An exception to this rule occurs, however, in the anhydrides of the fulgenic acids (Stobbe, *loc. cit.*).


$$\begin{array}{l}CMePh\colon C\cdot CO_2H\\ CMe_2\colon C\cdot CO_2H\end{array}$$

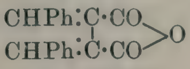
Colourless.


$$\left.\begin{array}{l}CMePh\colon C\cdot CO\\ CMe_2\colon C\cdot CO\end{array}\right>O$$

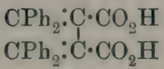
Sulphur yellow.


$$\begin{array}{l}CHPh\colon C\cdot CO_2H\\ CHPh\colon C\cdot CO_2H\end{array}$$

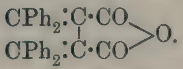
Colourless.


$$\left.\begin{array}{l}CHPh\colon C\cdot CO\\ CHPh\cdot C\cdot CO\end{array}\right>O$$

Lemon yellow.


$$\begin{array}{l}CPh_2\colon C\cdot CO_2H\\ CPh_2\colon C\cdot CO_2H\end{array}$$

Orange red.


$$\left.\begin{array}{l}CPh_2\colon C\cdot CO\\ CPh_2\colon C\cdot CO\end{array}\right>O.$$

Blood red.

There are probably two factors which bring about the increased tendency to produce colour in these anhydrides, firstly, the residual affinity of the carbonyl oxygens is now less completely satisfied and permits of their mutual attraction; and secondly, by the ring-formation the two carbonyl groups are drawn nearer together in space.

Another instance of a similar character may perhaps be noted in that diphenylfumaric acid is white; diphenylmaleic acid has not been isolated, but its anhydride is described as yellow with a greenish fluorescence.

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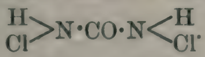
XXX.—*A Synthesis of para-Urazine from Carbamide.*

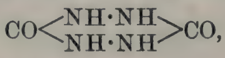
By FREDERICK DANIEL CHATTAWAY.

THE author has recently shown that two of the hydrogen atoms of carbamide can be replaced by chlorine, a dichlorocarbamide being formed. Although this compound, as might be expected, is very readily hydrolysed, it can be obtained by passing chlorine through a saturated aqueous solution of carbamide, when it crystallises out in small, transparent plates. It is safe to handle, and can be preserved for a considerable time in a dry atmosphere.

Its composition shows that it has the formula $CH_2ON_2Cl_2$, and having regard to its mode of formation as well as to the structure of carbamide itself, its constitution is undoubtedly represented by the formula  $\begin{smallmatrix}H\\Cl\end{smallmatrix}\!>\!N\cdot CO\cdot N\!<\!\begin{smallmatrix}H\\Cl\end{smallmatrix}$. As dichlorocarbamide thus contains two chlorine atoms, each attached to a nitrogen atom not otherwise linked to any complex organic group, and as it is a stable solid compound easily prepared and isolated and soluble in many common solvents, it promises to be of considerable use in organic synthesis.

When dichlorocarbamide is acted on by ammonia, a reaction takes place which is of interest, as it not only affords the first synthesis of *p*-urazine from carbamide itself, but adds another to the limited number of reactions by which nitrogen atoms can be made to link together.

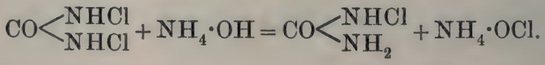
When dichlorocarbamide is added to a strong aqueous solution of ammonia, hydrolysis occurs accompanied by liberation of nitrogen and formation of ammonium carbonate, but, in addition, *p*-urazine,



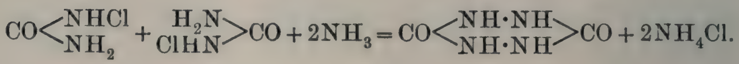
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot NH}\\ \mathrm{NH\cdot NH}\end{matrix}>\mathrm{CO},$$

is produced, and separates out in considerable quantity as a sparingly soluble, crystalline powder.

The formation of *p*-urazine from dichlorocarbamide in this reaction may be explained by assuming that by interaction with ammonium hydroxide one of the chlorine atoms is replaced by hydrogen * and a monochlorocarbamide produced, two molecules of which condense under the influence of the ammonia with elimination of hydrogen chloride, thus:



$$\mathrm{CO}<\begin{matrix}\mathrm{NHCl}\\ \mathrm{NHCl}\end{matrix}+\mathrm{NH_4\cdot OH}=\mathrm{CO}<\begin{matrix}\mathrm{NHCl}\\ \mathrm{NH_2}\end{matrix}+\mathrm{NH_4\cdot OCl}.$$



$$\mathrm{CO}<\begin{matrix}\mathrm{NHCl}\\ \mathrm{NH_2}\end{matrix}+\begin{matrix}\mathrm{H_2N}\\ \mathrm{ClHN}\end{matrix}>\mathrm{CO}+2\mathrm{NH_3}=\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot NH}\\ \mathrm{NH\cdot NH}\end{matrix}>\mathrm{CO}+2\mathrm{NH_4Cl}.$$

Curtius has shown that *p*-urazine, which he prepared from hydrazine hydrate,† can be heated on a water-bath with a mixture of equal parts of concentrated sulphuric acid and water for many hours without alteration. He found, however, that it could be converted into hydrazine and carbon dioxide by heating it with concentrated hydrochloric acid in a sealed tube to 150°.

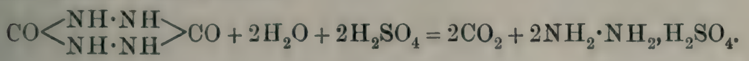
This hydrolysis can be much more easily effected by heating *p*-urazine with concentrated sulphuric acid to about 120—130°. Carbon dioxide is rapidly evolved, and hydrazine sulphate formed.

---

[*] This replacement of chlorine by hydrogen very frequently takes place when substituted nitrogen chlorides are treated with ammonia, ammonium hypochlorite or products of its decomposition being produced. That this replacement actually takes place in the reaction between dichlorocarbamide and ammonia is shown by the reconversion of a small amount of the dichlorocarbamide used into carbamide itself.

[†] *p*-Urazine was prepared by Curtius (*J. pr. Chem.*, 1895, [ii], **52**, 481) by acting on ethyl chloroformate in alcoholic solution with hydrazine hydrate, and then heating the ethyl hydrazinedicarboxylate, $N_2H_2(CO_2Et)_2$, formed with two molecules of hydrazine hydrate for some hours in a sealed tube at 100°.

The latter crystallises out in a pure state on cooling and adding a little water to the product :



$$\mathrm{CO}\Big<\begin{matrix}\mathrm{NH\cdot NH}\\ \mathrm{NH\cdot NH}\end{matrix}\Big>\mathrm{CO} + 2H_2O + 2H_2SO_4 = 2CO_2 + 2NH_2\cdot NH_2,H_2SO_4.$$

Dichlorocarbamide can be prepared from carbamide and converted into *p*-urazine so easily, and the latter can be so quickly hydrolysed, that the reactions afford a synthesis of hydrazine more adapted to prepare a small quantity of the pure sulphate than any yet described. The operations involved are simple, and excellently suited for showing the synthesis of hydrazine as a lecture experiment.

Preparation of p-*Urazine.*

In order to prepare *p*-urazine, it is not necessary to dry the dichlorocarbamide. The crude product, free from all adhering mother liquor, is dissolved in from ten to twenty times its weight of water and rapidly added to excess of concentrated ammonia, the mixture being thoroughly stirred. A vigorous evolution of nitrogen takes place, and a white, crystalline powder separates, a little more crystallises out on keeping, and a still further small quantity on evaporating the mother liquor after neutralising with hydrochloric acid. In the reaction nothing appears to be formed except nitrogen, ammonium carbonate, ammonium chloride, and *p*-urazine, but a small quantity of the dichlorocarbamide used is reconverted into carbamide. The yield of *p*-urazine is about 20 per cent. of the theoretical.

The *p*-urazine thus obtained as a white, crystalline powder can be crystallised from boiling water, in which it is sparingly soluble ; on cooling, it separates in small, colourless crystals, which melt, when rapidly heated, in the neighbourhood of 270°. The exact melting point of the pure substance cannot be determined, as the temperature at which liquefaction occurs varies considerably with the rate of heating, decomposition appearing to commence about 260°.

For analysis, the compound was recrystallised once from water :

0·1014 gave 41·8 c.c. N_2 (moist) at 12° and 755 mm. $N = 48·62$.

$C_2H_4O_2N_4$ requires $N = 48·28$ per cent.

Hydrolysis of p-*Urazine and Preparation of Hydrazine Sulphate.*

When *p*-urazine is mixed with about five times its weight of concentrated sulphuric acid and warmed to about 80°, it dissolves apparently without change ; on heating the solution to about 95—100°, hydrolysis slowly takes place, with evolution of carbon dioxide. On raising the temperature still higher, the rate of evolution of carbon dioxide increases, until at about 120—130° it is very rapidly liberated;* at this temperature hydrolysis is soon complete, and a clear, colourless liquid is obtained, which deposits crystals of hydrazine sulphate on cooling. It is best, however, to add to the cooled liquid its own bulk of water, when pure hydrazine sulphate at once separates as a white, crystalline powder. To ascertain its purity, a specimen was prepared as above, washed a few times with distilled water, dried, and analysed:

0·2406 gave 0·4298 $BaSO_4$. $H_2SO_4 = 75·06$.
N_2H_4,H_2SO_4 requires $H_2SO_4 = 75·37$ per cent.

The thanks of the author are due to Professor Odling, who has placed a laboratory at his disposal.

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XXXI.—*The Divergence of the Atomic Weights of the Lighter Elements from Whole Numbers.*

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WHY are the atomic weights of the first fifteen elements, expressed with reference to hydrogen as unit, slightly different from whole numbers, and why are they almost exactly whole numbers when expressed with reference to oxygen as 16? The present paper offers perhaps an explanation of these questions, and consequently may indicate how the hypothesis, first put forward by Prout, that the atoms of the elements are polymerides of the hydrogen atom, should be modified in order to make it possible to calculate accurately the weights of the lighter atoms.

The table on page 239 gives the atomic weights with reference to hydrogen, obtained by subtracting or adding to the nearest whole number a constantly increasing number of times a certain factor, namely, 0·0078; the agreement between these calculated atomic weights and the latest observed values is good.

Column I is the number of the element.

Column II gives the numbers 2N for "even" elements, and 2N + 1 for "odd" elements, that is, the whole numbers to which the atomic weights approximate.

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* Hydrazine sulphate is not appreciably oxidised by sulphuric acid until about 250°, at which temperature nitrogen and sulphur dioxide begin to be liberated.

Column III gives the factor, B, by which the constant, 0·0078, has to be multiplied; and B = A or A − 1.

Column IV represents the calculated atomic weights, and columns V and VI the latest observed values for the atomic weights (kindly given me by Dr. R. W. Gray, and taken from the table prepared by the International Committee for 1909; Ag = 107·88).

Table I

	I.	II.	III.	IV.*	V.	
Element.	N.	A.	B.	A ± B(0·0078).	H = 1.	O = 16.
Hydrogen	0	1	—	1·00	—	1·0078
	[1	3	2	2·9844	—	—]
Helium	2	4	4	3·9688	3·97	4
Lithium	3	7	6	6·9532	6·95	7·00
Glucinum	4	9	+8	9·0624	9·04	9·11
Boron	5	11	10	10·9220	10·91	11·0
Carbon	6	12	12	11·9064	11·907	12·00
Nitrogen	7	14	13	13·8986	13·898(6)	14·007
Oxygen	8	16	16	15·8752	15·8752	16·00
Fluorine	9	19	18	18·8596	18·86	19·00
Neon	10	20	20	19·8440	19·8(5)	20
Sodium	11	23	22	22·8284	22·82	23·00
Magnesium	12	24	+24	24·1872	24·13	24·32
Aluminium	13	27	26	26·7972	26·89	27·1
Silicon	14	23	+28	28·2184	28·08	28·3
Phosphorus	15	31	30	30·7660	30·76(6)	31·00

* Clarke has given 1·00779 as the atomic weight of hydrogen (O = 16), and, taking the constant as 0·0078, justifies these numbers being given to the fourth decimal place.

Thus the atomic weights are calculated from the formula: for "even" elements,

$$M = A \pm 0{\cdot}0978A, \text{ where } A = 2N;$$

for "odd" elements,

$$M = A \pm 0{\cdot}0078(A - 1), \text{ where } A = 2N + 1.$$

These results can be expressed in another way; for it appears that the atoms of these elements are direct polymerides of the hydrogen atom, but with a small portion of an atom left out or added. Now if the electron weighs about one-thousandth of that of the hydrogen atom, then 0·0078 would represent the weight of eight electrons.

The above relation may then be put as follows:

The atom of helium is 4 atoms of hydrogen, less 2 groups of 16 electrons.
,, ,, lithium is 7 ,, ,, ,, 3 ,, ,, ,,
,, ,, glucinum is 9 ,, ,, plus 4 ,, ,, ,,
,, ,, boron is 11 ,, ,, less 5 ,, ,, ,,
,, ,, carbon is 12 ,, ,, ,, 6 ,, ,, ,,
,, ,, nitrogen is 14 ,, ,, ,, 13 ,, 8 ,,
,, ,, oxygen is 16 ,, ,, ,, 8 ,, 16 ,,
,, ,, fluorine is 19 ,, ,, ,, 9 ,, ,, ,,

and so on.

It should be noticed that the whole number for nitrogen does not obey the formula $A = 2N + 1$, but $A = 2N$, although it is an "odd" element. The value of B, however, follows from that of A, and is not exceptional. In the case of glucinum we have again an exception to the formula $A = 2N$.

The formula suggests that an element of atomic weight, 2·9844, might exist, where $N = 1$ and $\quad = 3$.

Not quite such a simple relation could be found amongst the next series of elements, but after some search a fairly satisfactory relation was noticed, and is expressed in the following table:

TABLE II.

	I.	II.	III.	IV.	V.	VI.	VII.
						Observed.	
Element.	N.	A.	B.	C.	Calc. atomic weight.	H=1.	O=16.
Sulphur	16	32	−32	+10	31·8284	31·83	32·07
Chlorine......	17	35	+34	−10	35·1872	35·186	35·460
Argon.........	18	36+4	−36	−13	39·6178	39·61	39·92
Potassium ...	19	39	−38	+13	38·805	38·793	39·095
Calcium	20	40	−40	+13	39·7894	39·78	40·09
	21						
Scandium ..	22	44	−44	+13	43·7582	43·7(6)	44·1
	23						
Titanium ...	24	48	−48	+13	47·7270	47·7(3)	48·1
Vanadium ...	25	51	−50	+(2 × 13)	50·8128	50·8	51·2
Chromium ...	26	52	−52	+13	51·6958	51·69(7)	52·10
Manganese...	27	55	−54	−10	54·5008	54·50(5)	54·93
Iron	27	55	+54	0	55·4212	55·41(8)	55·85
	28						
Cobalt	29	59	−58	0	58·5476	58·54	59·0
Nickel	(29)	58	+58	−(2 × 13)	58·2496	58·23	58·68

Column IV represents the factor C in the following formulæ, by which the atomic weights are calculated:

for "even" elements,

$$M = A \pm 0{\cdot}0078(A \pm C), \text{ where } C = 10 \text{ or } 13;$$

for "odd" elements,

$$M = A \pm 0{\cdot}0078\{(A - 1) \pm C\}, \text{ where } C = 10 \text{ or } 13.$$

The relation $A = 2N$ for "even" and $A = 2N + 1$ for "odd" elements still holds.

Thus, according to the previous suggestion, the atom of sulphur would be 32 atoms of hydrogen less 16 groups of 16 electrons plus 10 groups of 8 electrons; the atom of chlorine would be 35 atoms of hydrogen plus 17 groups of 16 electrons less 10 groups of 8 electrons; the atom of potassium would be 39 atoms of hydrogen less 19 groups of 16 electrons plus 13 groups of 8 electrons, and so on.

It should be noted that the atom of argon must be regarded as composed of 36 atoms of hydrogen less 18 groups of 16 electrons less

13 groups of 8 electrons, but also with a nucleus of four hydrogen atoms added (compare helium 4).

Further, by assuming cobalt and nickel to have equal claim to the position of 29th element, their atomic weights may be shown to differ by the observed amount by calculating the atomic weight of cobalt according to the first simple formula given on page 239, and that of nickel by the second formula on page 240.

After nickel, the relation A = 2N, etc., breaks down, and one has no guide in finding the factor B. The relation A = 2N was first noticed by Rydberg (*Zeitsch. anorg. Chem.*, 1897, **14**, 66).

It should be pointed out that the same relation between the atomic weights can be arrived at from the mere fact of the atomic weights of most of the first fifteen elements being practically whole numbers when oxygen is taken as 16.

The formula used in changing from the one unit to the other is:

$$M_{H=1} = \frac{M_{O=16}}{1 + 0{\cdot}0078}.$$

If $M_{O=16}$ is a whole number, we may put M = 2N, where N is the number of the element as before.

Therefore
$$M_{H=1} = \frac{2N}{1{\cdot}0078},$$

and if $M_{H=1}$ is nearly a whole number, we have

$$M_{H=1} = 2N(1 - 0{\cdot}0078),$$

or

$$M_{H=1} = A - 0{\cdot}0078A\,;$$

and this is the formula previously obtained.

Thus, if the atomic weights of the elements obey this formula, they must be whole numbers with reference to oxygen as 16, and herein is an explanation of the fact that most of the first fifteen elements possess atomic weights which, expressed with reference to oxygen as 16, are almost exactly round numbers. Furthermore, if the atomic weights are expressed with reference to oxygen as 16, carbon as 12, etc., the atomic weight of hydrogen must be 1·0078.

The relation is consequently dependent on the ratio H : O = 1·0078 : 16; this ratio causing the rest of the elements to obey the relation, provided they have atomic weights which are whole numbers with reference to oxygen as 16. The relation, however, suggests the physical explanation of the departure from whole numbers when referred to hydrogen as unit.

In conclusion, it may be objected that by means of a "coarse and fine adjustment," practical identity may be arrived at between the calculated and found atomic weights of any element; or, indeed, between any two series of numbers. In general, this must be granted; but in the first series considered above, this empiricism is excluded by the fact that one of the factors mentioned on page 239 follows a nearly regular numerical series, namely, 2, 3, 4, 5, 6, 6½, 8, and 4½; the second factor is uniformly 16; whilst in the second series, given on page 240, the factors are uniformly 10 or 13. This also differentiates the scheme proposed from other devices for securing adherence to some formula, by which an approximation to the found values of the atomic weights can be arrived at.

The relation between the atomic weights, above set forth, if it be conceded that it expresses a truth, evidently strengthens the hypothesis that the elements are composed of one kind of matter. Hydrogen is the simplest known conglomeration of this matter. The position of hydrogen in the periodic table, standing alone as a link between the first and seventh groups, the existence of hydrogen in stars and nebulæ, and other considerations, first led me to examine the divergence of the atomic weights from whole numbers from the point of view of Prout's hypothesis.

The physical interpretation of the relation given is evidently not the only one that can be devised. Since the elements are built up by the conglomeration of the fundamental stuff, although not necessarily evolved in order of atomic weight, and since the atoms probably differ in internal structure, there are certain to be changes in the internal energy of the atoms, causing slight differences in mass. One would expect such changes to be proportional to the increase of the amount of the original stuff which conglomerates; the formula $M = A \pm A(0{\cdot}0078)$ agrees with this idea; and, further, it is conceivable that an increase in the size of an atom, due to addition of more matter, and the formation of a new atom, might either cause an increase or decrease of energy according to the configuration of the new atom; the positive and negative sign in the formula might thus be explained.

It is hoped that relations among the heavier atoms will eventually be found, but the uncertainty of finding the factor A, the inexactness with which the majority of the atomic weights of the heavier elements are as yet known, and the error caused by the reduction to the hydrogen scale, put difficulties in the way.

This relation is likely to prove most useful in determining the internal structure of an atom; but these indefinite and speculative physical interpretations of the formula are here put forward with all reserve.

I am greatly indebted to Sir William Ramsay for encouragement and advice; and my thanks are also due to Dr. Gray, Dr. T. C. Porter, and Miss Burke, who have given me much help.

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XXXII.—*The Constituents of the Bark of Prunus serotina. Isolation of* l-*Mandelonitrile Glucoside.*

By Frederick Belding Power and Charles Watson Moore.

The bark of *Prunus serotina*, Ehrhart (*Prunus virginiana*, Miller), commonly known as "Wild Cherry Bark," has long been used medicinally, and is recognised by both the United States and British Pharmacopœias. As it yields benzaldehyde and hydrocyanic acid in contact with water, it was quite naturally supposed to contain amygdalin or an analogous substance, although the attempts which have hitherto been made to isolate the cyanogenetic compound were unsuccessful. It had also been observed some years ago (*Pharm. Rundschau*, New York, 1887, **5**, 205) that the bark contains a fluorescent principle, but the identity or composition of this substance was not ascertained.

From the above considerations, it will be seen that, up to the present time, very little has been known regarding the more important constituents of wild cherry bark, and it was therefore deemed of interest to subject it to a complete chemical examination. Such an investigation appeared particularly desirable in view of the fact that, within the past few years, three isomeric mandelonitrile glucosides, $C_{14}H_{17}O_6N$, have been isolated from natural sources, and that one of these, *l*-mandelonitrile glucoside, was obtained from a closely-related species of *Prunus*, namely, *P. Padus*, Linné. The designations of the three isomeric glucosides, and the sources from which they were obtained, are as follows: "sambunigrin," from the leaves of the common black elder (*Sambucus nigra*, Linné), by Bourquelot and Danjou (*Compt. rend.*, 1905, **141**, 598; *Arch. Pharm.*, 1907, **245**, 202, 474); "prulaurasin," from the leaves of the cherry-laurel (*Prunus Lauro-cerasus*, Linné), by Hérissey (*Compt. rend.*, 1905, **141**, 959; *Arch. Pharm.*, 1907, **245**, 463, 473); and "amygdonitrile glucoside," from the young twigs of *Cerasus Padus*, Delarb. (*Prunus Padus*, Linné), by Hérissey (*Arch. Pharm.*, 1907, **245**, 475, 641; compare also Caldwell and Courtauld Trans., 1907, **91**, 671).

With regard to the relationship of the three above-mentioned compounds, namely, "sambunigrin," "prulaurasin," and "amygdonitrile glucoside" (*l*-mandelonitrile glucoside), it may be noted that they represent the β-glucosides of dextro-, racemic, and lævo-mandelonitrile respectively. Although *l*-mandelonitrile glucoside, frequently designated as "Fischer's glucoside," had been obtained by E. Fischer (*Ber.*, 1895, **28**, 1508), by Caldwell and Courtauld (Trans., 1907, **91**, 670), and by Auld (Trans., 1908, **93**, 1276), by the partial hydrolysis of amygdalin, its isolation by Hérissey (*loc. cit.*) was, until now, the only instance in which its occurrence in nature had been observed.

The present investigation of the bark of *Prunus serotina*, Ehrhart, has resulted in the isolation therefrom of *l*-mandelonitrile glucoside (m. p. 145—147°; $[\alpha]_D$ − 29·6°), which has also been obtained in the form of its tetra-acetyl derivative (m. p. 136—137°; $[\alpha]_D$ − 24°). This is, therefore, the second instance in which this glucoside has been observed to occur in nature. A summary of the results of the complete investigation of the bark, in the course of which a number of other substances have been isolated, is given at the end of this paper.

EXPERIMENTAL.

The material employed in the present investigation was obtained from the United States, and conformed in every respect to the description of the bark of *Prunus serotina*, Ehrhart, as recognised by the United States Pharmacopœia.

In order to determine the amount of hydrogen cyanide yielded by the bark, portions of 25 and 50 grams respectively of the finely-ground material were macerated with water for several days in a tightly-closed flask at a temperature of 20—25°. Steam was then passed through the mixture, and the distillate collected in a very dilute solution of sodium hydroxide. After the addition of a little sodium chloride, the product of distillation was titrated with a decinormal solution of silver nitrate. The amount of the latter solution required for 25 grams of bark was 3·4 c.c., and for 50 grams of bark, 7·0 c.c., thus corresponding to 0·0734 and 0·0756 per cent. of HCN respectively.

A portion of the bark was tested for the presence of an alkaloid, but with a negative result.

Fifty grams of the ground bark were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 110°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0·33 gram	= 0·66 per cent.
Ether	,,	2·47 ,,	= 4·94 ,,
Chloroform	,,	0·35 ,,	= 0·70 ,,
Ethyl acetate	,,	1·48 ,,	= 2·96 ,,
Alcohol	,,	3·53 ,,	= 7·06 ,,
	Total	8·16 grams	= 16·32 per cent.

For the purpose of a complete examination, a quantity (53·3 kilograms) of the ground bark was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 14·09 kilograms.

Distillation of the Extract with Steam. Separation of Benzoic Acid and an Essential Oil.

A quantity (4·5 kilograms) of the above-mentioned extract, representing about 17 kilograms of bark, was mixed with water, and steam passed through the mixture for several hours. The first portion of the distillate was tested for hydrogen cyanide, but with a negative result, thus affording evidence that no hydrolysis of the cyanogenetic glucoside had taken place in the process of distillation. The entire distillate, which amounted to about 8 litres, had an acid reaction, and contained some drops of oil floating on the surface. It was thoroughly extracted with ether, and the ethereal liquid shaken with a 5 per cent. solution of sodium carbonate. On acidifying the alkaline liquid, a substance separated in small, glistening plates, which, after recrystallisation from hot water, melted at 119—120°:

0·1665 gave 0·4210 CO_2 and 0·0785 H_2O. $C = 68·9$; $H = 5·2$.

$C_7H_6O_2$ requires $C = 68·8$; $H = 4·9$ per cent.

This substance was thus identified as benzoic acid, and the amount obtained was 3 grams.

The ethereal liquid, from which the benzoic acid had been extracted as above described, was washed, dried, and the ether removed, when a small amount (2·7 grams) of an essential oil was obtained. This oil had an agreeable, aromatic odour, quite distinct from that of benzaldehyde. It distilled between 100° and 120°/15 mm. as a pale yellow liquid, which, at 4°, deposited a very small quantity of a crystalline substance. The amount of essential oil was too small for its further examination.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as above described, there remained in the distillation flask a quantity of a green resin (A) and a dark-coloured, aqueous liquid. The latter was separated by filtration while still hot, and the green resin repeatedly treated with boiling water until nothing further was removed. The aqueous liquid and washings from the green resin were united, and allowed to stand for several days, when a quantity of a brown resin (B) slowly separated. This was removed from the liquid, and thoroughly washed with cold water, the washings being added to the aqueous liquid, which may be designated as (C).

Examination of the Green Resin (A).

This resin at the ordinary temperature was a dark green, waxy solid, and amounted to 180 grams. It was dissolved in alcohol and mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with the following solvents: petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Green Resin.

This extract was a dark green, viscous liquid, and amounted to 80 grams. It was dissolved in ether, the ethereal solution being extracted with successive portions of aqueous sodium carbonate, and finally washed with water. The alkaline liquids and washings were united, acidified, and extracted with ether, when 27 grams of a viscid, oily liquid were obtained. On distilling this liquid under diminished pressure, it passed over between 215° and 270°/10 mm., and then became almost solid. It consisted of a mixture of fatty acids, which were examined in connexion with a similar product obtained from the non-acidic portion of the petroleum extract after its hydrolysis.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The ethereal liquid which had been extracted with sodium carbonate, as above described, was subsequently shaken with a solution of sodium hydroxide, which, however, removed nothing. The ether was then evaporated, when a quantity (40 grams) of an oily product was obtained. This was hydrolysed by heating with an alcoholic solution of potassium hydroxide, the alcohol removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a brown, crystalline product was obtained. This was distilled under diminished pressure, and then crystallised from a mixture of ethyl acetate and dilute alcohol, when it separated in fine, glistening, flat needles melting at 135—136°. The amount of this substance was 7 grams. After drying at 110°, it was analysed:

0·1342 gave 0·4100 CO_2 and 0·1474 H_2O. C = 83·3 ; H = 12·2.

$C_{27}H_{46}O$ requires C = 83·9 ; H = 11·9 per cent.

This substance thus agrees in composition with a phytosterol, and it yielded the colour reactions of this class of compounds. A determination of its rotatory power gave the following result:

0·2450, dissolved in 25 c.c. of chloroform, gave α_D − 0°40′ in a 2-dcm. tube, whence $[\alpha]_D$ − 34·0°.

The acetyl derivative, when crystallised from acetic anhydride, separated in needles melting at 118—119°.

0·2160, dissolved in 25 c.c. of chloroform, gave α_D $-0°34'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-32·8°$.

The above-mentioned phytosterol was tested for the presence of stigmasterol, $C_{30}H_{50}O$, according to the method described by Windaus and Hauth (*Ber.*, 1907, **40**, 3681), and was found to be free from the latter compound. The melting point of its acetate would indicate that it is not identical with sitosterol (*Zeitsch. physiol. Chem.*, 1902, **34**, 461), but it agrees closely in its character with the phytosterol obtained from olive bark (Trans., 1908, **93**, 909).

Identification of the Fatty Acids.

The alkaline, aqueous solution of potassium salts from which the phytosterol had been removed by extraction with ether, as above described, was acidified, and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A quantity (12 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 215° and 270°/10 mm. As these acids distilled within the same range of temperature as those previously obtained, which existed in the bark in a free state, for the purpose of their examination the two portions were mixed.

Twenty grams of the total mixed acids were converted into their lead salts, and the latter digested with ether, when a portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure, when in each case they amounted to about 8 grams. The acids obtained from the soluble portion of lead salt were liquid, whilst those from the insoluble portion were solid.

The Liquid Acids.—These acids were fractionally distilled under diminished pressure, and the following fractions collected: (*a*) 214—216° (about 5 grams); (*b*) 216—230°/12 mm. (about 2 grams). They were analysed and their iodine values determined, with the following results:

(*a*) 0·1730 gave 0·4855 CO_2 and 0·1784 H_2O. C = 76·5; H = 11·4.
0·4190 absorbed 0·6312 iodine. Iodine value = 150·6.

(*b*) 0·1890 gave 0·5360 CO_2 and 0·1930 H_2O. C = 77·3; H = 11·3.
0·2152 absorbed 0·3372 iodine. Iodine value = 156·7.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Iodine value = 90·1.
$C_{18}H_{32}O_2$ „ C = 77·1; H = 11·4 „ „ = 181·4.

These results indicated that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, the latter predominating.

In order to obtain more definite information respecting the composition of the above mixture of unsaturated acids, the remaining portions of the two fractions (6 grams) were united, and oxidised in alkaline solution with potassium permanganate in the cold. On subsequently treating the mixture with a slight excess of sulphur dioxide, a white precipitate was produced, which was collected and digested with much ether. This removed about 0·2 gram of an acid melting at 128°, which was evidently dihydroxystearic acid, and its formation confirmed the presence of oleic acid in the mixture. The portion of the white precipitate which was not dissolved by the ether was almost completely soluble in hot water, from which, on cooling, a quantity (1·2 grams) of a crystalline substance separated, which melted at 158—160°:

0·0895 gave 0·2042 CO_2 and 0·0845 H_2O. $C=62·2$; $H=10·5$.
$C_{18}H_{36}O_6$ requires $C=62·1$; $H=10·3$ per cent.

This substance was a tetrahydroxystearic acid, and the amount obtained confirmed the previous indication of a predominating proportion of linolic acid in the original mixture.

The acid, aqueous liquid, which was separated by filtration from the above-mentioned white precipitate of oxidation products, was evaporated to dryness, and the residue extracted with alcohol. A very small amount (0·1 gram) of an acid melting at 168—170° was thus obtained. This was evidently a hexahydroxystearic acid (*iso*linusic acid), and its formation indicated the presence of a small proportion of *iso*linolenic acid, $C_{18}H_{30}O_2$, in the original mixture.

The Solid Acids.—These acids were fractionally crystallised from glacial acetic acid, but both the first and last fractions, (*a*) and (*b*), melted at about 56—58°, and possessed practically the same composition:

(*a*) 0·1320 gave 0·3670 CO_2 and 0·1520 H_2O. $C=75·8$; $H=12·8$.
(*b*) 0·1160 „ 0·3225 CO_2 „ 0·1325 H_2O. $C=75·8$; $H=12·7$.
$C_{16}H_{32}O_2$ requires $C=75·0$; $H=12·5$ per cent.
$C_{18}H_{36}O_2$ „ $C=76·1$; $H=12·7$ „

As it was evident that no separation of the acids had been effected by crystallisation, a portion of the mixture was fractionally precipitated in the form of silver salts:

I. 0·1560 gave, on ignition, 0·0445 Ag. Ag = 28·5.
II. 0·1570 „ „ „ 0·0450 Ag. Ag = 28·7.
III. 0·1700 „ „ „ 0·0490 Ag. Ag = 28·8.
$C_{16}H_{31}O_2Ag$ requires $Ag=29·8$ per cent.
$C_{18}H_{35}O_2Ag$ „ $Ag=27·6$ „

The above results indicated that the solid acids consisted of a mixture of palmitic and stearic acids in about equal proportions.

Ethereal Extract of the Green Resin. Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

This extract was a brown, amorphous mass, and amounted to 50 grams. It was redissolved in about 1 litre of warm ether, and the ethereal solution allowed to stand for several days, when a very small amount (0·5 gram) of a grey precipitate was slowly deposited. This was collected and crystallised several times from a mixture of pyridine and dilute alcohol, when 0·2 gram of a substance was obtained which, under the microscope, was seen to consist of small rosettes of needles. It melted between 285° and 290°:

0·1178 gave 0·3125 CO_2 and 0·1130 H_2O. C = 72·3; H = 10·7.

$C_{23}H_{40}O_4$ requires C = 72·6; H = 10·5 per cent.

The substance yielded a colour reaction similar to that produced by the phytosterols. Thus, when dissolved in chloroform with a little acetic anhydride, and a drop of sulphuric acid subsequently added, a pink colour was produced, which rapidly changed to blue, and finally to green. When heated with acetic anhydride, an acetyl derivative was obtained which separated in leaflets melting at 160°.

The above results rendered it evident that the substance in question was ipuranol, a dihydric alcohol, which was first obtained in these laboratories from *Ipomoea purpurea*, Roth, and this has subsequently been isolated from nutmeg and from olive bark (*Amer. J. Pharm.*, 1908, **80**, 264, 576; Trans., 1908, **93**, 907).

The ethereal solution from which the ipuranol had been deposited, as above described, was shaken with several successive portions of aqueous sodium carbonate and finally washed with water. A quantity of a black, insoluble sodium compound was thus obtained, which, when acidified, yielded a quantity of resinous substance. As nothing definite could be directly separated from it, the substance was dissolved in alcohol, a little water added, and such an amount of sulphuric acid that the latter represented 5 per cent. of the mixture. The whole was then heated for several hours in a reflux apparatus, and the mixture subsequently distilled with steam, but no volatile product was obtained. There remained in the distillation flask a brown, aqueous liquid, together with a dark-coloured, resinous mass. The latter was collected, mixed with purified sawdust, and the thoroughly-dried mixture extracted with light petroleum. This removed about 10 grams of a viscid liquid, which, when distilled under diminished pressure, passed over between 210° and 220°/15 mm. as a clear, pale yellow oil, amounting to about 5 grams. This oily liquid dissolved in warm alkali hydroxide, the solution becoming gelatinous on cooling. On allowing the oily liquid to stand for a few days, it deposited a very small amount of a saturated acid, which, after recrystallisation, melted at 50—55°. The liquid portion was unsaturated, and its analysis and determination of the iodine value gave the following results:

0·1273 gave 0·3565 CO_2 and 0·1390 H_2O. C = 76·4; H = 12·1.

0·1976 absorbed 0·1563 iodine. Iodine value = 79·1.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Iodine value = 90·1.

These results indicated that the oily liquid consisted to a large extent of oleic acid, which must have existed in the resin in the form of an ester other than a glyceride, although such an occurrence of oleic acid appears hitherto not to have been recorded.

The acid, aqueous liquid contained in the distillation flask, from which the above-described resinous material had been removed, was treated with baryta for the removal of the sulphuric acid. The filtered liquid, after concentration under diminished pressure, reduced Fehling's solution, and yielded a small amount of *d*-phenylglucosazone, melting at 206—208°. It was thus apparent that at least a portion of the above-described ethereal extract of the resin was glucosidic.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Green Resin. *Isolation of β-Methylaesculetin.*

These extracts all consisted of brown, resinous material, and amounted to 9, 16, and 20 grams respectively. As nothing of a definite nature could be isolated from them by the ordinary methods, they were united and heated for several hours in a reflux apparatus with dilute alcohol containing 5 per cent. of its weight of sulphuric acid. After the addition of water and the removal of the alcohol by distillation with steam, there remained in the distillation flask a brown, aqueous liquid, together with a quantity of resinous material. Nothing could be isolated from the resin, but on repeatedly extracting the acid, aqueous liquid with ether, a small quantity (0·3 gram) of a crystalline substance was obtained. This substance melted at 204°, and its solution in alkalis exhibited a fine blue fluorescence:

0·1272 gave 0·2920 CO_2 and 0·0484 H_2O. C = 62·6; H = 4·2.

$C_{10}H_8O_4$ requires C = 62·5; H = 4·2 per cent.

This substance was thus identified as β-methylæsculetin. Further quantities of it were subsequently obtained from the brown resin (B), and from the original aqueous liquid designated as (C), after hydrolysis with dilute sulphuric acid.

Examination of the Brown Resin (B).

This was a dark brown powder, and amounted to 171 grams. It was dissolved in alcohol, and mixed with purified sawdust, the thoroughly-dried mixture being then successively extracted in a Soxhlet apparatus with the following solvents: ether, chloroform, ethyl acetate, and alcohol.

Ethereal Extract of the Brown Resin.

This extract consisted of brown, resinous material, and amounted to only 15 grams. As nothing definite could be obtained from it by the usual methods or by extraction with alkalis, it was heated in a reflux apparatus with dilute alcohol containing 5 per cent. of its weight of sulphuric acid. After the addition of water, and the removal of the alcohol, a small amount of soft, resinous material was deposited. This was extracted with light petroleum, when a product was obtained which, after distillation under diminished pressure, yielded 5 grams of a liquid fatty acid. The latter was analysed, and its iodine value determined, with the following results:

0·1243 gave 0·3540 CO_2 and 0·1344 H_2O. $C=77·7$; $H=12·0$.

0·2030 absorbed 0·1829 iodine. Iodine value $=$ 90·1.

$C_{18}H_{34}O_2$ requires $C=76·6$; $H=12·1$ per cent. Iodine value $=$ 90·1.

This liquid acid evidently consisted for the most part of oleic acid, with a small amount of some substance of higher carbon content.

Chloroform Extract of the Brown Resin.

This was a light brown resin, which amounted to only 2 grams. It was redissolved in chloroform, and the solution extracted with several portions of aqueous sodium hydroxide. The combined alkaline liquids were acidified and extracted with chloroform, when about 0·1 gram of a crystalline substance was obtained. This substance melted at 204°, and was identified as β-methylæsculetin, which, in the present instance, was evidently contained in the bark in a free state and not in the form of its glucoside.

Ethyl Acetate and Alcohol Extracts of the Brown Resin.

Both these extracts consisted of brown, resinous material, and they amounted to about 15 grams and 140 grams respectively. As nothing definite could be obtained from them by the ordinary methods, they were united, and heated for several hours in a reflux apparatus with dilute alcohol containing 5 per cent. of its weight of sulphuric acid. The mixture was then diluted with water, and the alcohol removed by distillation with steam, when there remained in the distillation flask a red, aqueous liquid and a quantity of finely-divided red resin. The latter, when collected and dried, amounted to 150 grams.

The above-mentioned red, aqueous liquid on extraction with ether yielded 0·4 gram of β-methylæsculetin. After this treatment the sulphuric acid was removed by means of baryta, and the filtered liquid concentrated under diminished pressure. It was found to contain sugar, since it readily reduced Fehling's solution and yielded *d*-phenylglucosazone, melting at 205—206°.

The red, resinous material above described was only partly soluble in alcohol. The soluble portion was mixed with purified sawdust, and the thoroughly-dried mixture successively extracted in a Soxhlet apparatus with light petroleum and chloroform.

Petroleum Extract of the Red Resin.—This extract was very small in amount, and from it only a little phytosterol (m. p. 128—130°) was obtained.

Chloroform Extract of the Red Resin.—This extract was likewise small in amount. It was redissolved in chloroform, and the solution extracted with aqueous sodium hydroxide. On acidifying the alkaline solution, a product was obtained which, when recrystallised from alcohol, melted at 204°, and was identified as β-methylæsculetin. The amount of the latter substance obtained from this source was 1·3 grams, and it is probable that it was produced by the hydrolysis of some methylæsculin which had been occluded in the brown resin, for the aqueous liquid (C), subsequently to be described, yielded after hydrolysis a relatively large quantity of β-methylæsculetin, which undoubtedly was present in the form of its glucoside.

Fusion of the Insoluble Red Resin with Potassium Hydroxide.—As noted above, only a portion of the red, resinous material was soluble in alcohol. Of the insoluble portion, 25 grams were reduced to powder, and gradually introduced into 150 grams of potassium hydroxide in a state of fusion, the temperature of the mixture being maintained at 240—260° for a considerable time. After cooling, the mass was dissolved in water, the solution acidified with sulphuric acid, and distilled with steam. The distillate contained a quantity of volatile acid, which was converted into a barium salt, the latter amounting to 10 grams. On examining this salt, it was ascertained that the volatile acid consisted largely of acetic acid, with a relatively small proportion of formic and butyric acids.

After the removal of the volatile acids by distillation with steam, as above described, the contents of the distillation flask were extracted with ether. This removed about 5 grams of a crystalline substance which, after repeated crystallisation from water, melted at 196—198°:

0·1252 gave 0·2510 CO_2 and 0·0470 H_2O. C = 54·7; H = 4·2.

$C_7H_6O_4$ requires C = 54·5; H = 3·9 per cent.

This substance was thus identified as protocatechuic acid.

Examination of the Aqueous Liquid (C).

This liquid, as already indicated, represented that portion of the original alcoholic extract of the bark which was soluble in cold water, and from which the previously-described resins (A) and (B) had been removed.

Isolation of Benzoic Acid.

The aqueous liquid was extracted many times with ether, the combined ethereal liquids being washed, dried, and the solvent removed. A quantity of a crystalline product was thus obtained, which was subjected to vigorous distillation with steam. The distillate had a distinctly acid reaction, and, on extraction with ether, yielded 9 grams of a crystalline substance melting at 120—121°:

0·1432 gave 0·3608 CO_2 and 0·0661 H_2O. C = 68·7; H = 5·1.

$C_7H_6O_2$ requires C = 68·8; H = 4·9 per cent.

This substance thus proved to be benzoic acid, and its identity was further confirmed by the formation of its methyl ester, boiling at 197—198°.

Isolation of Trimethylgallic Acid.

After completely removing the benzoic acid from the crystalline product by distillation with steam, as above described, the contents of the distillation flask were extracted with ether, and the ethereal liquid shaken with eight successive portions of a dilute solution of ammonium carbonate. The liquids obtained by the first three extractions with alkali gave, on acidification, a distinctly crystalline precipitate, and these were therefore united. The liquids obtained by the subsequent five extractions, when acidified, yielded a more or less amorphous precipitate, and this was separately examined, as described below.

The precipitate obtained by acidifying the liquids from the first three ammonium carbonate extractions was crystallised from ethyl acetate, when it yielded 10 grams of a crystalline compound melting at 165—169°. After several recrystallisations from the same solvent, the melting point remained constant at 167—169°:

0·1647 gave 0·3424 CO_2 and 0·0865 H_2O. C = 56·7; H = 5·8.

$C_{10}H_{12}O_5$ requires C = 56·6; H = 5·6 per cent.

This substance is evidently trimethylgallic acid, and its isolation is of considerable interest from the fact that, so far as known to us, it is the first instance in which its occurrence in nature has been observed.

Further confirmation of the identity of the above substance was afforded by the preparation of some derivatives, a determination of the number of methoxyl groups, and its molecular weight. The methyl ester was prepared in the usual manner, and, as this can be volatilised with steam, it affords a ready method for the purification of the acid. When crystallised from water, it separated in long needles melting at 84°:

0·2098 gave 0·4485 CO_2 and 0·1190 H_2O. C = 58·3; H = 6·3.

$C_{11}H_{14}O_5$ requires C = 58·4; H = 6·2 per cent.

The acid was regenerated from this ester, and crystallised from ethyl acetate, when it melted at 167—169°, as before, and was again analysed:

0·1287 gave 0·2680 CO_2 and 0·0685 H_2O. C = 56·8; H = 5·9.

$C_{10}H_{12}O_5$ requires C = 56·6; H = 5·6 per cent.

The *silver* salt was obtained as a crystalline precipitate by the addition of silver nitrate to a solution of the ammonium salt. It was washed with a little cold water, dried in a vacuum over sulphuric acid, and analysed:

0·5070 gave, on ignition, 0·1710 Ag. Ag = 33·7.

$C_{10}H_{11}O_5Ag$ requires Ag = 33·8 per cent.

A determination of the number of methoxyl groups in the acid by Perkin's modification of the Zeisel method gave the following result:

0·1316 gave 0·4370 AgI. OMe = 43·8.

$C_7H_3O_2(OMe)_3$ requires OMe = 43·9 per cent.

The molecular weight of the acid was determined by the cryoscopic method in acetic acid solution:

0·2965 in 22·2415 of acetic acid gave $\Delta t - 0{\cdot}254°$. M.W. = 201.

$C_{10}H_{12}O_5$ requires M.W. = 212.

Isolation of p-*Coumaric Acid.*

After the removal of the trimethylgallic acid from the ethereal liquid by the first three extractions of the latter with aqueous ammonium carbonate, as above described, the subsequent extractions with this alkali gave, when acidified, about 8 grams of a product melting at 210—213° with evolution of carbon dioxide. This was recrystallised from hot water, from which it separated in small, colourless needles melting, as before, at 210—213°:

0·1580 gave 0·3810 CO_2 and 0·0690 H_2O. C = 65·8; H = 4·9.

$C_9H_8O_3$ requires C = 65·9; H = 4·9 per cent.

This substance was thus identified as *p*-coumaric acid. Further confirmation of its identity was obtained by methylating a portion of the acid, when the methyl derivative, $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}C_2H_2{\cdot}CO_2H$ (m. p. 170°), and its methyl ester, $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}C_2H_2{\cdot}CO_2{\cdot}CH_3$ (m. p. 88—90°), were obtained.

The aqueous liquid, from which the three above-mentioned acids had been obtained by extraction with ether, was concentrated under diminished pressure to a volume of about 6 litres, and treated with a solution of basic lead acetate. This produced a voluminous, yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture, a liquid was obtained which gave a bluish-black coloration with ferric chloride, and evidently contained a quantity of tannin, but nothing crystalline could be separated from it.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a volume of about 1·5 litres. This liquid, on cooling, formed a gelatinous mass, which again became fluid on warming or on dilution with water or alcohol. The nature of the substance to which the gelatinisation of the liquid was due could not be ascertained. The liquid contained a cyanogenetic glucoside, together with a sugar which yielded *d*-phenylglucosazone, melting at 208—210°.

With the object of isolating the cyanogenetic compound from the above-mentioned aqueous liquid, the latter was divided into two equal portions. One of these portions, amounting to 800 grams, was mixed with purified sawdust, and the thoroughly-dried mixture extracted for eight days in a Soxhlet apparatus with dry ethyl acetate. As the cyanogenetic compound could not be separated from the resulting extract, the latter was mixed with a small quantity of sawdust, and extracted for three days with boiling chloroform, but this treatment removed only traces of the glucoside. The chloroform extract was therefore washed with a little water, then shaken with a dilute solution of sodium hydroxide to remove any acidic or phenolic substances, and, finally, the solvent evaporated. A very small amount (about 0·01 gram) of a crystalline substance was thus obtained, which, after recrystallisation from a mixture of chloroform and ether, melted sharply at 240—241°, but could not be further examined.

In order to ascertain the amount of cyanogenetic glucoside in the aqueous liquid, 25 grams of the remaining portion of the latter were treated with emulsin, when 0·0783 gram of hydrogen cyanide was evolved, which would correspond to 0·8555 gram of a compound having the molecular weight of mandelonitrile glucoside. The amount of such a glucoside in the total aqueous liquid (1600 grams), representing 4·5 kilograms of the original alcoholic extract or 17 kilograms of bark, would thus have been about 55 grams, or 0·32 per cent. of the weight of the bark.

Although the above attempts to isolate the cyanogenetic compound from the aqueous liquid were unsuccessful, it was subsequently obtained from the original alcoholic extract of the bark by a special method, which will be described below.

Isolation of β-Methylaesculetin.

A quantity (100 grams) of the above-mentioned aqueous liquid was diluted with water to the measure of about 500 c.c., then 25 grams of sulphuric acid added, and the mixture boiled for several hours. Steam was subsequently passed through the mixture in order to remove any volatile products formed by the hydrolysis. The contents of the distillation flask were then filtered, the acid, aqueous liquid being extracted first with ether, and subsequently with chloroform. After the removal of the respective solvents, residues were obtained which were separately dissolved in about 10 c.c. of water. On keeping these solutions overnight, they deposited small quantities of a substance which, when crystallised from alcohol, melted constantly at 204°, and was identified as β-methylæsculetin. The amount of this substance thus obtained was 0·4 gram, which would correspond to 6·4 grams from the total aqueous liquid, the latter representing about 17 kilograms of bark. As the β-methylæsculetin was obtained from this liquid only after hydrolysis, it is highly probable that it existed in the form of its glucoside, methylæsculin, and the corresponding amount of the latter compound would be about 12 grams, or 0·07 per cent. of the weight of the bark.

On boiling the β-methylæsculetin for about ten minutes with acetic anhydride, its *acetyl* derivative was formed. This compound is only sparingly soluble in cold acetic anhydride, from which it separates in colourless leaflets, melting at 176—177°:

0·1140 gave 0·2564 CO_2 and 0·0460 H_2O. C = 61·3; H = 4·5.

$C_{10}H_7O_4(CO{\cdot}CH_3)$ requires C = 61·5; H = 4·3 per cent.

In extracting the β-methylæsculetin from the hydrolysed aqueous liquid by means of ether, as above described, it was observed that the ethereal liquid also contained a small amount of an acidic substance which was readily soluble in water. A further quantity of this substance was obtained, and its identification effected, as described below.

Isolation of l-*Mandelic Acid.*

A quantity (400 grams) of the previously-mentioned aqueous liquid was diluted with water to the measure of 1 litre, 50 grams of sulphuric acid added, and the mixture boiled for six hours. It was then subjected to distillation with steam, when the distillate was found to contain small amounts of furfuraldehyde, benzaldehyde, and benzoic acid. The aqueous, acid liquid remaining in the distillation flask, after being allowed to cool, was filtered, and extracted twelve times with ether. The ethereal liquid from the first extraction was discarded as being likely to contain a little benzoic acid. All the subsequent extractions were united, and the solvent removed, when a residue was obtained which was mixed with 50 c.c. of water. On allowing the liquid to stand for some time, a quantity of β-methylæsculetin was deposited, which was removed by filtration, and the strongly acid, aqueous filtrate extracted five times with ether. The ethereal liquid was then repeatedly extracted with small quantities of a dilute solution of ammonium carbonate until the aqueous liquids just began to show an alkaline reaction. The combined ammonium carbonate extracts were acidified with hydrochloric acid and extracted with ether, when about 3 grams of a crystalline substance were obtained, melting at 128—130°. After recrystallisation from benzene, it melted at 130—133°:

0·1238 gave 0·2880 CO_2 and 0·0624 H_2O. C = 63·4; H = 5·6.

The substance was again crystallised from benzene, when it melted at 132—133°, and was again analysed:

0·1276 gave 0·2965 CO_2 and 0·0635 H_2O. C = 63·4; H = 5·5.

$C_8H_8O_3$ requires C = 63·2; H = 5·3 per cent.

0·3710, dissolved in 20 c.c. of water, gave in a 2-dcm. tube $\alpha_D - 5°44'$, whence $[\alpha]_D - 154·5°$.

The substance was thus identified as *l*-mandelic acid, and its isolation from the aqueous liquid, after hydrolysis, afforded evidence of the presence of either amygdalin or *l*-mandelonitrile glucoside.

Isolation of l-*Mandelonitrile Glucoside.*

One kilogram of the original alcoholic extract, representing about 3·8 kilograms of the bark, was mixed with 2 litres of water, and the volatile constituents were removed by distillation with steam. The contents of the distillation flask were then filtered while hot from the previously-described green resin, the latter being thoroughly washed with water, and the washings added to the filtrate. After allowing the combined aqueous filtrate and washings to stand for several weeks, a quantity of the previously-described brown resin was deposited, from which the clear liquid was decanted. This liquid, being large in amount, was divided into four portions, each of which was concentrated as far as possible under diminished pressure. To each portion 200 c.c. of alcohol were then added, and, after complete solution, the thin syrups were again concentrated under diminished pressure, this operation being repeated until the mass became too viscid for further concentration. Each portion was then dissolved in 200 c.c. of absolute alcohol, and to the thin syrups so obtained 1 litre of boiling, dry ethyl acetate was added in each case. After standing for several hours, the liquids were decanted from the precipitated syrup, concentrated to about 100 c.c., and, while still hot, 500 c.c. of boiling, dry ethyl acetate added to each portion. They were again allowed to stand for several hours, when some syrupy material was deposited, from which the clear ethyl acetate liquids were decanted. These were then united, concentrated to the measure of 500 c.c., and, after cooling, 500 c.c. of dry ether added. The clear liquid was then separated, the solvent completely removed, and the residue dissolved in about 300 c.c. of cold water. This aqueous liquid was shaken with small successive portions of ether in order to remove the acids which were known to be present, after which it was treated with a solution of normal lead acetate until no further precipitate was produced. The yellow precipitate was removed by filtration with the aid of the pump, and the aqueous filtrate concentrated on the water-bath under diminished pressure to about 30—40 c.c. A mixture of 300 c.c. of alcohol and 300 c.c. of ethyl acetate was then added, and the whole allowed to stand overnight. The clear liquid, decanted from a small amount of a yellow precipitate, was concentrated to a small volume, the residual product being then dissolved in water and treated with hydrogen sulphide for the removal of the lead. After filtration, the aqueous liquid was concentrated under diminished pressure to the measure of about 50 c.c., when an excess of calcium carbonate was added to neutralise the free acetic acid, and the mass then extracted with alcohol. This alcoholic extract was evaporated to dryness on a water-bath under diminished pressure, and the residue dissolved in ethyl acetate, when, after concentrating the solution to about 20 c.c., the glucoside slowly crystallised in small, colourless needles. It was recrystallised from ethyl acetate, when two crops of crystals were obtained. The first fraction of crystals, which amounted to 0·6 gram, melted initially at 144—146°, and, after further crystallisation, at 145—147°. The second fraction of crystals, which was very small in amount (about 0·1 gram), was somewhat less pure, and melted at 135—140°. Both these fractions, when treated with emulsin, yielded hydrogen cyanide, benzaldehyde, and glucose. The first fraction was analysed, with the following result:

0·1392 gave 0·2904 CO_2 and 0·0750 H_2O. C = 56·9; H = 6·0.

$C_{14}H_{17}O_6N$ requires C = 56·9; H = 5·8 per cent.

0·3605, dissolved in 20 c.c. of water, gave in a 2-dcm. tube α_D − 1°4′, whence $[\alpha]_D$ − 29·6°.

The above-described cyanogenetic compound was thus identified as *l*-mandelonitrile glucoside.

A determination of the specific rotatory power of the small fraction of glucoside melting at 135—140° gave the following result:

0·0956, dissolved in 20 c.c. of water, gave in a 2-dcm. tube α_D − 0°14′, whence $[\alpha]_D$ − 24·4°.

Tetra-acetyl-l-*mandelonitrile Glucoside.*—In the preliminary attempts to obtain the cyanogenetic glucoside from wild cherry bark a method was employed which, although not resulting in the isolation of the glucoside itself, led to the preparation of its acetyl derivative. This method varied from that above described for the isolation of the glucoside at the stage when the yellow precipitate produced by normal lead acetate was obtained. After the removal of this precipitate by filtration, the filtrate was treated with hydrogen sulphide for the removal of the lead, again filtered, and the liquid concentrated to about 200 c.c. It was then repeatedly extracted with hot amyl alcohol, the temperature of the mixture being kept at about 80°. By this means the glucoside was separated from the last traces of sugar, after which the solvent was removed by distillation in a rapid current of steam. The aqueous liquid contained in the distillation flask was then concentrated to the consistency of a thick syrup, the latter boiled for an hour with twenty times its weight of acetic anhydride, and the product poured into water. After allowing the mixture to stand for some hours, it was extracted with ether, the ethereal liquid being subsequently shaken with a 5 per cent. solution of sodium hydroxide in order to remove small amounts of acidic substances, and afterwards washed with water. On concentrating the ethereal liquid to a small bulk and allowing it to stand, the acetyl derivative of the glucoside separated in long needles. It was twice crystallised from alcohol, when it melted at 136—137°. The amount of this derivative obtained from 1 kilogram of the alcoholic extract, representing about 3·8 kilograms of the bark, was 0·6 gram:

0·1458 gave 0·3025 CO_2 and 0·0740 H_2O. C = 56·6; H = 5·6.

$C_{22}H_{25}O_{10}N$ requires C = 57·0; H = 5·4 per cent.

0·3470, dissolved in 20 c.c. of ethyl acetate, gave in a 2-dcm. tube α_D − 0°50′, whence $[\alpha]_D$ − 24·0°.

The *l*-mandelonitrile glucoside is accompanied in the wild cherry bark by an enzyme, which may be obtained by adding to a cold aqueous infusion of the bark a large volume of strong alcohol. The precipitate thus produced is a light-coloured, amorphous powder, readily soluble in cold water. It contains a large proportion of inorganic material, but readily hydrolyses β-glucosides.

Summary.

The results of this investigation may be summarised as follows :

The material employed, consisting of the air-dried bark of *Prunus serotina*, Ehrhart, yielded on maceration with water an amount of hydrogen cyanide corresponding to about 0·075 per cent. of its weight. It contains a relatively small amount of a cyanogenetic glucoside, which has been shown to be *l*-mandelonitrile glucoside, $C_{14}H_{17}O_6N$ (m. p. 145—147° ; $[\alpha]_D$ $-29·6°$), and the latter has also been obtained in the form of its tetra-acetyl derivative (m. p. 136—137° ; $[\alpha]_D$ $-24·0°$). An enzyme which hydrolyses β-glucosides is also present in the bark.

An alcoholic extract of the bark, when distilled with steam, yielded small amounts of benzoic acid and an essential oil, but no hydrogen cyanide. The essential oil distilled between 100° and 120°/15 mm., and possessed an odour quite distinct from that of benzaldehyde. The non-volatile constituents of the bark, as obtained after treating the alcoholic extract with steam, consisted of a green resin, insoluble in either hot or cold water; a brown resin, readily soluble in the hot aqueous liquid, but which was slowly deposited on standing ; and material which remained dissolved in the cold aqueous liquid. The green resin, amounting to about 1 per cent. of the weight of the bark, yielded a phytosterol, $C_{27}H_{46}O$ (m. p. 135—136° ; $[\alpha]_D$ $-34·0°$) ; palmitic, stearic, oleic, and linolic acids, with apparently a very little *iso*linolenic acid ; a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$, melting at 285—290° ; and, after acid hydrolysis, oleic acid, dextrose, and β-methylæsculetin, $C_{10}H_8O_4$ (m. p. 204°). The brown resin, likewise amounting to about 1 per cent. of the weight of the bark, yielded, after acid hydrolysis, a trace of a phytosterol, small amounts of oleic acid, β-methylæsculetin, and dextrose, together with insoluble, red, resinous material, which, on fusion with potassium hydroxide, gave formic, acetic, butyric, and protocatechuic acids. The portion of the alcoholic extract of the bark which was soluble in cold water, and from which the above-described resins had been removed, contained *l*-mandelonitrile glucoside, together with a quantity of sugar and tannin. It yielded, furthermore, benzoic, trimethylgallic, and *p*-coumaric acids, traces of a substance melting at 240—241°, and, after heating with dilute sulphuric acid, *l*-mandelic acid and β-methylæsculetin were obtained. The two latter compounds were evidently formed by the hydrolysis of *l* mandelonitrile glucoside and methylæsculin respectively.

In conclusion, the authors desire to express their thanks to Dr. S. J. M. Auld for having kindly provided them with a small specimen of *l*-mandelonitrile glucoside, obtained by the partial hydrolysis of amygdalin.

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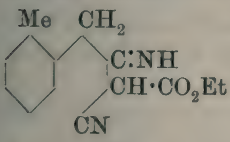
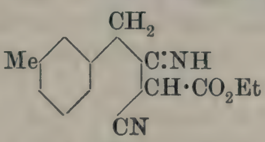
XXXIII.—*The Formation and Reactions of Imino-compounds. Part VIII. The Formation of Methyl Derivatives of 2-Phenyl-1 : 3-naphthylenediamine from the Three Tolylacetonitriles.*

By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

In a former communication (Trans., 1907, **91**, 1687) dealing with the behaviour of ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate (I), ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate (II), and ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate (III) towards cold concentrated sulphuric acid, it was shown that the position of the methyl group exerted a remarkable effect on their transformation into ethyl 1-methyl-5 : 7-naphthylenediamine-6-carboxylate (IV), ethyl 2-methyl-5 : 7-naphthylenediamine-6-carboxylate (V), and ethyl 2-methyl-6 : 8-naphthylenediamine-7-carboxylate (VI) respectively.



(I.)



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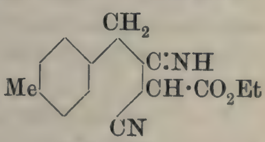

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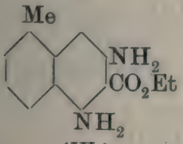

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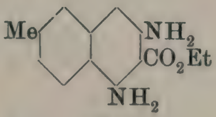
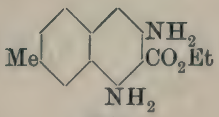


(V.)



(VI.)

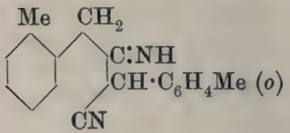
Thus from the ortho- (I) and para- (II) derivatives only a small yield of the corresponding naphthalene derivatives was obtained, whereas the transformation of the meta-compound (III) was almost quantitative. It was suggested at the time (*loc. cit.*, p. 1695) that, as regards the ortho- and para-imino-nitriles, it was evidently the meta-position of the methyl group, with respect to the carbon atom at which ring formation was bound to ensue, which exerted a hindering effect on the formation of the naphthalene ring; because in the case of the meta-derivative, in which ring formation was proved to take place at the carbon atom in the para-position with respect to the methyl group, no hindrance was apparent. In order to gain further evidence on this point, we have therefore studied the intramolecular condensation of the three tolylacetonitriles (compare Trans., 1907, **91**, 1282), and have obtained *β-imino-α-cyano-αγ-di-*o*-tolylpropane* (VII), *β-imino-α-cyano-αγ-di-*m*-tolylpropane* (VIII), and *β-imino-α-cyano-αγ-di-*p*-tolylpropane* (XI).

During the preparation of these compounds it was at once apparent that the presence of the methyl group in the three tolylacetonitriles also exerted a marked effect on the formation of the imino-nitriles.

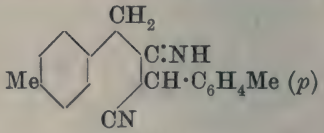
The same influence had been noticed in the condensation of the three tolylacetonitriles with ethyl cyanoacetate (Trans., 1907, **91**, 1687), for in these cases it was found that, whereas the *o*- and *p*-tolylacetonitriles gave a yield of about 40 per cent. of the condensation products, *p*-tolylacetonitrile gave as much as 60—65 per cent. of the theoretical amount.

In just the same way *p*-tolylacetonitrile undergoes almost complete intramolecular condensation, and scarcely any unchanged nitrile can be recovered from the product, whilst under the most favourable conditions the imino-nitriles from *o*- and *m*-tolylacetonitrile cannot be obtained in yields greater than 35—40 per cent. of the theoretical quantity.

The hindering influence of the position of the methyl group on the formation of the naphthalene ring when this group is in the meta-position with respect to the carbon atom at which ring formation must ensue is again clearly indicated by the behaviour of the three β-imino-α-cyano-αγ-ditolylpropanes towards concentrated sulphuric acid; thus, β-imino-α-cyano-αγ-di-*o*-tolylpropane (VII) and β-imino-α-cyano-αγ-di-*p*-tolylpropane (VIII), compounds in which ring formation has to take place in the meta-position with respect to the methyl group, yield, on treatment with sulphuric acid, scarcely 10 per cent. of the theoretical quantity of 6-o-*tolyl*-1-*methyl*-5:7-*naphthylene*-

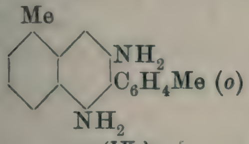


(VII.)

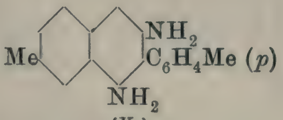


(VIII.)

diamine (IX) and 7-p-*tolyl*-2-*methyl*-6 : 8-*naphthylenediamine* (X) respectively.

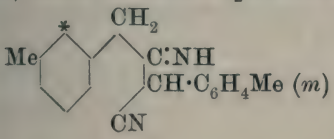


(IX.)

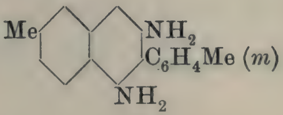


(X.)

On the other hand, β-imino-α-cyano-αγ-di-*m*-tolylpropane (XI) gives as much as 80 per cent. of 6-m-*tolyl*-2-*methyl*-5 : 7-*naphthylenediamine* (XII) under the same experimental conditions.



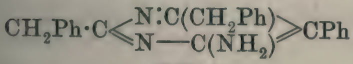
(XI.)



(XII.)

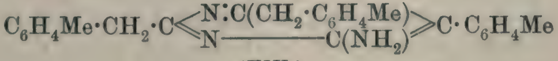
The ring formation in this case is represented as taking place in the para-position with respect to the methyl group in the benzene ring, although it is, of course, possible that it might ensue in the ortho-position to this group, marked in the above formula by an asterisk. The point was dealt with in a former paper (Trans., 1907, **91**, 1692) regarding the transformation of ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate into ethyl 2-methyl-5 : 7-naphthalenediamine-6-carboxylate, and the position of the methyl group was proved by the oxidation of the naphthalene derivative to 4-methylphthalic acid by means of chromic acid. The formation of the same acid from the base derived from β-imino-α-cyano-αγ-di-*m*-tolylpropane under the same experimental conditions clearly showed the correctness of the formula given above.

During the course of this investigation considerable quantities of the methyl derivatives of pyrimidine, analogous to cyanbenzyline, have been isolated. Cyanbenzyline (6-amino-5-phenyl-2 : 4-dibenzylpyrimidine) (XIII) is formed when phenylacetonitrile is treated either in alcoholic solution with sodium ethoxide or in xylene solution with metallic sodium (compare Trans., 1906, **89**, 1931 ; 1907, **91**, 1287), and in the same way the three 6-amino-5-tolyl-2 : 4-dimethylbenzylpyrimidines of the general formula (XIV) have been isolated.



$$CH_2Ph\cdot C\left<\begin{matrix}N{:}C(CH_2Ph)\\ N—C(NH_2)\end{matrix}\right>CPh$$

(XIII.)



$$C_6H_4Me\cdot CH_2\cdot C\left<\begin{matrix}N{:}C(CH_2\cdot C_6H_4Me)\\ N——C(NH_2)\end{matrix}\right>C\cdot C_6H_4Me$$

(XIV.)

The intramolecular condensations of the three nitriles were carried out both in xylene solution by means of "molecular" sodium and in alcohol solution in the presence of sodium ethoxide, but in the former case a small quantity of alcohol was added to the xylene, since it had been found (Trans., 1908, **93**, 176) that the presence of traces of sodium ethoxide materially increases the quantities of imino-nitrile formed.

The pyrimidine derivative is produced to a very much greater extent in the alcohol experiment than in xylene, and is usually separated in a crystalline condition from the solution on cooling. On the other hand, the xylene experiment yields the larger quantity of imino-nitrile, but scarcely any of the pyrimidine derivative.

It is worthy of note that, whereas the pyrimidine derivatives are formed in considerable quantities from *o*- and *p*-tolylacetonitrile, *m*-tolylacetonitrile yields only a very small quantity of this substance.

EXPERIMENTAL.

The Intramolecular Condensation of the Three Tolylacetonitriles.

The imino-nitriles from the three tolylacetonitriles can be prepared either by the action of "molecular" sodium on a xylene solution of the tolylacetonitrile containing a trace of alcohol, or by the action of sodium ethoxide on an alcoholic solution of the nitrile. Since the methods adopted were the same in the case of the three nitriles, it will be sufficient to describe the details of the processes once only.

In Xylene Solution.—5·7 Grams of sodium were melted under a little xylene contained in a small flask, and brought to a fine state of division by shaking. The xylene was then poured off, the finely-divided sodium washed with dried xylene, and finally mixed with 75 c.c. of the hydrocarbon containing 1 c.c. of ethyl alcohol. Sixty-five grams of the tolylacetonitrile were then added, and the mixture was heated on the water-bath until all sodium had passed into solution. Water was then added, and, after having been acidified by means of acetic acid, the whole was distilled in a current of steam until all xylene and unchanged tolylacetonitrile had passed over. The residue was extracted with ether, the ethereal solution vigorously shaken with dilute hydrochloric acid to remove the pyrimidine derivative, then with dilute sodium carbonate solution, and finally dried and evaporated. The imino-nitrile was further purified by distillation under diminished pressure.

In Alcohol Solution.—5·7 Grams of sodium were dissolved in 70 grams of alcohol, and the solution mixed with 65 grams of the tolylacetonitrile, the mixture being heated on the water-bath for two hours. In spite of the fact, already mentioned, that the three tolylacetonitriles condense with themselves with varying degrees of readiness, it was not found possible to increase the yield by prolonging the above reaction, since in all three cases further heating merely led to the "alcoholysis" of the unchanged nitrile with the formation of ethylamine. The alcoholic solution, after being heated for the above length of time, deposited in all three cases a quantity of the crystalline pyrimidine derivative on cooling. This was collected by filtration, and the alcoholic solution, after being mixed with water and acidified with acetic acid, was distilled in a current of steam until all unchanged tolylacetonitrile had passed over. The residue was then extracted with ether, the ethereal solution washed with dilute hydrochloric acid to remove any remaining pyrimidine derivative, and then with dilute sodium carbonate, being finally dried and distilled free from ether. The imino-nitrile was purified by distillation under diminished pressure.

Of the two methods, that carried out in xylene solution is to be recommended if the imino-nitrile is the product desired, since less of the pyrimidine derivative is formed under these conditions, and the end-point of the reaction is easily ascertained by the fact that all sodium has passed into solution; moreover, there is little or no tendency for the unchanged nitrile to "alcoholyse" under the conditions of the experiment. If, however, the pyrimidine derivative is desired, the method involving the use of alcoholic sodium ethoxide is the most suitable.

β-Imino-α-cyano-αγ-di-o-tolylpropane, $C_6H_4Me\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot C_6H_4Me$.

The crude imino-nitrile, prepared by either of the above processes, is a viscid liquid which, on rapid distillation, yields a fraction boiling at 270—280°/18 mm.:

0·1922 gave 0·5793 CO_2 and 0·1211 H_2O. C = 82·20; H = 7·0.

$C_{18}H_{18}N_2$ requires C = 82·4; H = 6·9 per cent.

The compound is a thick syrup which shows no signs of solidifying. Its constitution was proved by the following experiment: Five grams of the imino-nitrile were added to an alcoholic solution of one and a-half times the calculated quantity of potassium hydroxide, and the solution boiled on the water-bath until the odour of ammonia was no longer apparent. Water was then added and the alcohol evaporated, when the solution, on being acidified, gave a crystalline precipitate which, when recrystallised from water, yielded long needles melting at 88°:

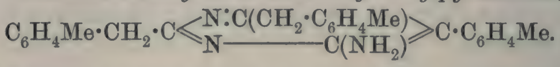
0·1876 gave 0·4937 CO_2 and 0·1167 H_2O. C = 71·78; H = 6·91.

$C_9H_{10}O_2$ requires C = 72·00; H = 6·7 per cent.

The compound is therefore *o*-tolylacetic acid, $C_6H_4Me\cdot CH_2\cdot CO_2H$.

The yield of the pure imino-nitrile represented 40 per cent. of the theory. It was thought that the low-boiling fraction, which distilled fairly constantly at 235—240°/18 mm., might contain the ketone corresponding with the imino-nitrile. This substance might be expected to have been formed during the process of the condensation, since in the analogous experiment with phenylacetonitrile under similar conditions considerable quantities of *a*-cyanodibenzyl ketone were isolated. No crystalline product, however, could be obtained from the low-boiling fraction, and the amount of substance at our disposal was too small for an extended investigation.

6-*Amino*-5-o-*tolyl*-2 : 4-*di*-o-*methylbenzylpyrimidine*,



$$C_6H_4Me\cdot CH_2\cdot C\Big\langle\begin{array}{l}N{:}C(CH_2\cdot C_6H_4Me)\\ N\text{————}C(NH_2)\end{array}\Big\rangle C\cdot C_6H_4Me.$$

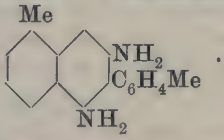
This substance is precipitated in a crystalline condition during the process of the condensation of *o*-tolylacetonitrile by means of alcoholic sodium ethoxide, and can be obtained by filtering the solution before distilling in steam. It is, moreover, recovered in the xylene experiment on washing an ethereal solution of the product, after steam distillation, with dilute hydrochloric acid. During this process the hydrochloride of the pyrimidine derivative, which is insoluble in dilute hydrochloric acid, forms a third layer in the separating funnel midway between the ethereal solution and the aqueous layer. It can, therefore, be readily separated and converted into the free base by warming on the water-bath with dilute sodium carbonate solution. The pyrimidine derivative obtained in this way separates from alcohol in small, colourless needles melting at 140—141°:

0·1835 gave 0·5540 CO_2 and 0·1144 H_2O. C = 82·35 ; H = 6·92.

$C_{27}H_{27}N_3$ requires C = 82·4 ; H = 6·9 per cent.

The base is similar in its properties to cyanbenzyline, and when treated with concentrated hydrochloric acid forms a gummy hydrochloride which could not be obtained crystalline.

6-o-*Tolyl*-1-*methyl*-5 : 7-*naphthylenediamine*,



In order to prepare this substance, five grams of *β*-imino-*a*-cyano-*aγ*-di-*o*-tolylpropane were mixed with 30 grams of cold concentrated sulphuric acid, and the dark red solution was kept at the ordinary temperature for five minutes. On pouring the strongly acid solution on ice, a small quantity of a bulky precipitate separated, which was filtered and the clear filtrate rendered alkaline with ammonia. The oil which separated set to a resin on cooling, and when crystallised from methyl alcohol yielded colourless plates melting at 136°:

0·1845 gave 0·5569 CO_2 and 0·1184 H_2O. C = 82·3; H = 7·1.

$C_{18}H_{18}N_2$ requires C = 82·4; H = 6·9 per cent.

The base is readily soluble in ethyl and methyl alcohol, benzene or chloroform, and sparingly so in light petroleum (b. p. 60—70°), from which solvent it can, however, be crystallised. It rapidly becomes coloured red on exposure to the air, and is obtained in yields amounting to about 10 per cent. of the theory. The other products of the reaction are the bulky precipitate already mentioned, due evidently to the presence of some *α*-cyano-di-*o*-methyldibenzyl ketone in the imino-compound used, and a phenolic base, which is precipitated with the naphthalene derivative, but is insoluble in methyl alcohol.

This compound is evidently analogous to the similar compounds obtained in the transformation of ethyl *β*-imino-*α*-cyano-*γ*-*o*-tolylbutyrate and ethyl *β*-imino-*α*-cyano-*γ*-*p*-tolylbutyrate into the corresponding naphthalene derivatives (compare Trans., 1907, **91**, 1694); their constitutions have not yet been determined.

The *dihydrochloride*, $C_{18}H_{18}N_2,2HCl$, is precipitated on adding concentrated hydrochloric acid to a cold solution of the base in alcohol. It forms colourless plates from concentrated hydrochloric acid:

0·2178 gave 0·1849 AgCl. Cl = 21·00.

$C_{18}H_{18}N_2,2HCl$ requires Cl = 21·19 per cent.

The *diacetyl* derivative, $C_{18}H_{16}N_2(Ac)_2$, is prepared by the action of acetyl chloride on the base. One gram was boiled with acetyl chloride on the water-bath until all had passed into solution, when excess of chloride was removed by evaporation. The diacetyl derivative remained as a colourless, gummy mass, which became solid on rubbing with alcohol. On recrystallisation from alcohol, it formed microscopic needles melting at 245°:

0·1901 gave 0·5303 CO_2 and 0·1095 H_2O. C = 76·07; H = 6·4.

$C_{22}H_{22}O_2N_2$ requires C = 76·3; H = 6·3 per cent.

*β-Imino-α-cyano-αγ-di-*m*-tolylpropane,*

$C_6H_4Me{\cdot}CH_2{\cdot}C(:NH){\cdot}CH(CN){\cdot}C_6H_4Me$.

When prepared by either of the methods given on page 264, this imino-nitrile is a viscid oil, which, when rapidly distilled, gives a principal fraction boiling at 275—280°/18 mm.:

0·1762 gave 0·5309 CO_2 and 0·1115 H_2O. C = 82·17; H = 7·03.

$C_{18}H_{18}N_2$ requires C = 82·4; H = 6·9 per cent.

As in the case of its isomeride, this substance is a viscid, colourless oil which could not be obtained crystalline. In order to prove its constitution, 5 grams were dissolved in alcohol and added to an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, the mixture being heated on the water-bath until the odour of ammonia ceased to be apparent. The solution was then freed from alcohol by evaporation, and acidified by means of hydrochloric acid. The resulting white precipitate yielded colourless needles melting at 61° when recrystallised from water:

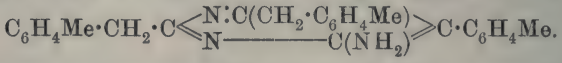
0·2011 gave 0·5294 CO_2 and 0·1229 H_2O. $C=71·82$; $H=6·79$.

$C_9H_{10}O_2$ requires $C=72·00$; $H=6·7$ per cent.

The compound is therefore *m*-tolylacetic acid, $C_6H_4Me\cdot CH_2\cdot CO_2H$.

The yield of the imino-nitrile is about the same as in the case of the ortho-derivative, being about 38 per cent. of the theory. Only a small quantity of low-boiling fraction was obtained, from which, however, no definite product could be isolated.

6-*Amino*-5-m-*tolyl*-2 : 4-*di*-m-*methylbenzylpyrimidine*,



$$C_6H_4Me\cdot CH_2\cdot C\left\langle\begin{array}{l}N\colon C(CH_2\cdot C_6H_4Me)\\ N\text{————————}C(NH_2)\end{array}\right\rangle C\cdot C_6H_4Me.$$

This compound is formed with very much less readiness than either the ortho- or para-derivative. A small quantity is precipitated in a crystalline condition during the intramolecular condensation of *m*-tolylacetonitrile in the presence of sodium ethoxide, and a further quantity can be obtained on washing the product from the "xylene" experiment with dilute hydrochloric acid. The base derived from the latter experiment was, however, always obtained as a viscid oil which showed no tendency to crystallise, and it was only after some crystals had been obtained in the "alcohol" experiment, which started crystallisation when added to the oil, that it could be induced to solidify. The compound crystallises from alcohol in small needles melting at 147°, but it will only separate in the crystalline form when a crystal is present; in fact, the compound exhibits very little tendency to crystallise:

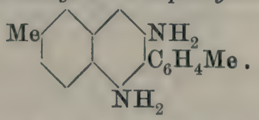
0·1834 gave 0·5549 CO_2 and 0·1136 H_2O. $C=82·52$; $H=6·88$.

$C_{27}H_{27}N_3$ requires $C=82·4$; $H=6·9$ per cent.

The base shows the characteristic property of these compounds, namely, when mixed with concentrated hydrochloric acid it at once becomes gummy.

The *hydrochloride*, $C_{27}H_{27}N_3,HCl$, can be obtained in a crystalline condition by adding concentrated hydrochloric acid to a cold solution of the base in alcohol, when it separates after some time in colourless needles.

6-m-*Tolyl-2-methyl*-5 : 7-*naphthylenediamine*,



This base, which is formed in larger yields than either the ortho- or para-derivatives, is best prepared in the following way: Five grams were added to well-cooled concentrated sulphuric acid, and the dark-coloured solution was allowed to remain at the ordinary temperature for ten minutes. At the end of this time, it was poured on ice, and the solution freed from a small quantity of insoluble matter by filtration. The clear solution on being rendered alkaline with ammonia, deposited an oil which set to a resin on cooling. Although readily soluble in methyl alcohol, the compound could not be separated in a crystalline condition, and it was only after the solution had remained for some weeks that crystals were ultimately obtained. The base forms slightly coloured, small plates melting at 143°:

0·1853 gave 0·5577 CO_2 and 0·1172 H_2O. C = 82·07; H = 7·02.

$C_{18}H_{18}N_2$ requires C = 82·4; H = 6·9 per cent.

The compound rapidly becomes coloured red on exposure, and is obtained in yields of about 80 per cent. It is the most difficult to obtain crystalline of all the bases of this type yet investigated; 2-phenyl-1 : 3-naphthylenediamine itself, as well as the methyl derivatives described in this communication, are all precipitated in a resinous condition, but, excepting the meta-compound mentioned above, they can all easily be obtained in a crystalline form. For working with these compounds it is not, however, necessary to use the crystalline substance, since the resins are quite pure if they are obtained by adding water to a clear alcoholic solution of the base.

The resin when set can be ground to a powder and dried in just the same way as a crystalline solid. The following analysis of the resin derived from the meta-compound in this way illustrates the above point:

0·1747 gave 0·5262 CO_2 and 0·1107 H_2O. C = 82·13; H = 7·04.

$C_{18}H_{18}N_2$ requires C = 82·4; H = 6·9 per cent.

The *dihydrochloride*, $C_{18}H_{18}N_2,2HCl$, can be obtained in white, microscopic needles on dissolving the base in concentrated hydrochloric acid and keeping the solution for some time:

0·2135 gave 0·1811 AgCl. Cl = 20·99.

$C_{18}H_{18}N_2,2HCl$ requires Cl = 21·19 per cent.

The *diacetyl* derivative, $C_{18}H_{16}N_2(Ac)_2$, can be prepared by boiling the base with acetyl chloride until all has dissolved, and then evaporating the excess of chloride on the water-bath. The diacetyl derivative remains as a colourless gum, which, when dissolved in alcohol and the solution diluted with water, yields colourless needles melting at 235°:

0·1861 gave 0·5195 CO_2 and 0·1876 H_2O. C = 76·14; H = 6·40.

$C_{22}H_{22}O_2N_2$ requires C = 76·3; H = 6·3 per cent.

Oxidation of 6-m-*tolyl*-2-*methyl*-5 : 7-*naphthylenediamine to* 4-*Methylphthalic Acid.*—This oxidation was carried out in order to establish the constitution of this naphthalene derivative, since, although it was very probable that ring formation would ensue in the para-position with respect to the methyl group in the same way as in the case of ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate (Trans., 1907, **91**, 1705), yet it was possible that in the present case ring formation might take place in the ortho-position with respect to the methyl group with the formation of 7-*m*-tolyl-1-methyl-6 : 8-naphthylenediamine. The oxidation was effected in the same way as described in the case of ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate. Ten grams of the base were dissolved in excess of dilute sulphuric acid and the solution heated to boiling. Twenty-five grams of potassium dichromate were then dissolved in water and the two hot solutions mixed, the whole being finally heated for a few minutes on the sand-bath. The dark-coloured precipitate was then filtered and dried on a porous plate, after which it was extracted thoroughly with ether.

The substance insoluble in ether was then boiled with sodium carbonate solution and filtered, when the alkaline solution, on acidifying, deposited a solid acid which crystallised from water in colourless prisms melting at 152°:

0·1992 gave 0·5243 CO_2 and 0·1216 H_2O. C = 71·78; H = 6·78.

$C_9H_{10}O_2$ requires C = 72·0; H = 6·7 per cent.

The acid is therefore 4-methylphthalic acid (compare Niementowski, *Monatsh.*, 1891, **12**, 624, and Young, *Ber.*, 1892, **25**, 2108). The acid was further characterised by converting it by means of acetyl chloride into its anhydride melting at 92°.

β-*Imino-α-cyano-αγ-di*-p-*tolylpropane*,
$C_6H_4Me\cdot CH_2\cdot C(:NH)\cdot CH(CN)\cdot C_6H_4Me$.

p-Tolylacetonitrile undergoes intramolecular condensation much more readily than either its ortho- or meta-isomeride, and when either of the methods described on p. 264 are employed, scarcely any unchanged nitrile is recovered from the product. When the condensation is carried out in alcohol solution, about one-third of the product consists of the pyrimidine derivative, and the reaction is characterised by the fact that when the nitrile is added to the solution of sodium ethoxide, an intense purple colour is produced, which, however, disappears on heating. When xylene is the solvent used, scarcely any of the pyrimidine derivative is formed, and the imino-nitrile is obtained in yields representing 85 per cent. of the theoretical. When prepared by either method the imino-nitrile is a viscid oil, which distils without appreciable decomposition at 280—283°/18 mm. as a colourless syrup showing no tendency to crystallise:

0·1850 gave 0·5562 CO_2 and 0·1169 H_2O. $C = 81{\cdot}98$; $H = 7{\cdot}02$.

$C_{18}H_{18}N_2$ requires $C = 82{\cdot}4$; $H = 6{\cdot}9$ per cent.

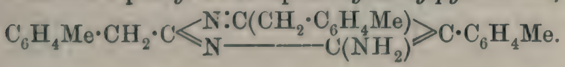
The constitution of the compound was proved, as in the previous cases, by alkaline hydrolysis, but much greater difficulty was met with in this instance in bringing about the fission of the chain than in any of the other cases recorded. The complete hydrolysis was, however, ultimately effected in the following way: Five grams were added to an alcoholic solution containing three times the calculated quantity of potassium hydroxide contained in a reflux apparatus, and the mixture was heated on the water-bath for twenty-four hours. At the end of this time, water was added, and the solution further heated on the sand-bath until the odour of ammonia was no longer apparent, when dilute hydrochloric acid was added, and the oily mass which separated was extracted with ether. The ethereal extract was then shaken with sodium carbonate solution, and the alkaline extract acidified. In this way a white solid was obtained which, when recrystallised from water, yielded colourless needles melting at 91°:

0·1916 gave 0·5039 CO_2 and 0·1173 H_2O. $C = 71{\cdot}72$; $H = 6{\cdot}80$.

$C_9H_{10}O_2$ requires $C = 72{\cdot}0$; $H = 6{\cdot}7$ per cent.

The acid is therefore *p*-tolylacetic acid, $C_6H_4Me\cdot CH_2\cdot CO_2H$.

6-*Amino*-5-p-*tolyl*-2 : 4-*di*-p-*methylbenzylpyrimidine*,



$$C_6H_4Me\cdot CH_2\cdot C\Big\langle\begin{matrix}N\colon C(CH_2\cdot C_6H_4Me)\\ N\text{————}C(NH_2)\end{matrix}\Big\rangle C\cdot C_6H_4Me.$$

This compound is not precipitated during the condensation of *p*-tolylacetonitrile in alcoholic solution, as is the case with the ortho- and meta-derivatives, and has to be extracted from the ethereal solution of the condensation product, after distillation with steam, by means of hydrochloric acid (see p. 266). The hydrochloric acid washings yield the pyrimidine base, on treatment with sodium carbonate solution, as a white, crystalline precipitate, which, when recrystallised from either methyl alcohol or light petroleum (b. p. 70—80°), yields colourless, concentric needles melting at 117—120°. The melting point is not sharp, but repeated recrystallisation from light petroleum fails to alter it:

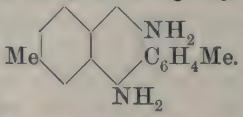
0·1888 gave 0·5705 CO_2 and 0·1165 H_2O. C = 82·40 ; H = 6·85.

$C_{27}H_{27}N_3$ requires C = 82·4 ; H = 6·9 per cent.

When added to concentrated hydrochloric acid the crystalline base at once forms an insoluble gum.

The *hydrochloride*, $C_{27}H_{27}N_3,HCl$, can be obtained in a crystalline condition by adding a little concentrated hydrochloric acid to a solution of the base in alcohol, and allowing the solution to stand. It forms white needles.

7-p-*Tolyl*-2-*methyl*-6 : 8-*naphthylenediamine*,



The yield of this base from the imino-nitrile is scarcely more than 9 per cent. of the theory, the method found most convenient for its formation being as follows: Ten grams of β-imino-α-cyano-αγ-di-*p*-tolylpropane were added to 60 grams of well-cooled concentrated sulphuric acid, and the dark red solution, after being kept at the ordinary temperature for fifteen minutes, was poured on ice. The aqueous solution was then filtered from a small quantity of insoluble matter, and the filtrate rendered alkaline with ammonia, when a large quantity of resinous matter was precipitated. On treatment with hot methyl alcohol, only a small portion of this dissolved, and the solution on filtering and cooling deposited the base in colourless, glistening plates melting at 160° :

0·1828 gave 0·5542 CO_2 and 0·1080 H_2O. C = 82·67 ; H = 6·5.

$C_{18}H_{18}N_2$ requires C = 82·4 ; H = 6·9 per cent.

The base becomes coloured red on exposure to the air, and is appreciably less soluble in solvents than the ortho- or meta-derivatives. The compound insoluble in methyl alcohol mentioned above, which is the chief product of the reaction, evidently belongs to the same series as those prepared under similar conditions from compounds in which the formation of the naphthalene ring is also hindered. Their nature has not as yet been determined.

The *dihydrochloride*, $C_{18}H_{18}N_2,2HCl$, is prepared by dissolving the base in concentrated hydrochloric acid and allowing the solution to stand. It forms colourless plates :

0·2284 gave 0·1940 AgCl. Cl = 21·01.

$C_{18}H_{18}N_2,2HCl$ requires Cl = 21·19 per cent.

The *diacetyl* derivative, $C_{18}H_{16}N_2(Ac)_2$, is best prepared by the action of acetyl chloride. The base was boiled with this substance until all had passed into solution, when the diacetyl derivative remained as a viscid gum on evaporating the excess of chloride on the water-bath. It separates slowly from dilute alcohol in clusters of microscopic needles, melting at 176° :

0·1768 gave 0·4941 CO_2 and 0·1027 H_2O. C = 76·21 ; H = 6·45.

$C_{18}H_{18}N_2$ requires C = 76·3 ; H = 6·4 per cent.

Much of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

THE UNIVERSITY,
MANCHESTER.

XXXIV.—*Formation of Heterocyclic Compounds. Part I.* 1-*Phenylpyrrolidine*-2 : 5-*dicarboxylic Acid from Adipic Acid.*

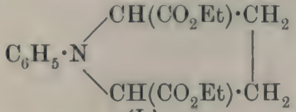
By HENRY RONDEL LE SUEUR.

CONSIDERABLE quantities of muconic acid being required for an investigation in connexion with this substance, the action of diethylaniline on ethyl αδ-dibromoadipate was tried, in the hope that two molecules of hydrogen bromide would be eliminated from the latter substance with production of the ester of the desired acid. It was soon seen, however, that the action of diethylaniline in this case was not the normal one, as a considerable quantity of ethyl bromide was liberated during the reaction. Since ethyl bromide was also obtained by the action of diethylaniline on methyl αδ-dibromoadipate, it was clear that the ethyl group arose from the diethylaniline and not from the ester. This led to the study of the action of monoethylaniline on ethyl αδ-dibromoadipate, and the results obtained form the subject of this communication.

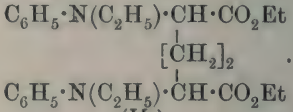
The action of diethylaniline on ethyl αδ-dibromoadipate is being studied fully, and the results obtained will be communicated in due course.

Ethyl αδ-dibromoadipate has been prepared previously by Willstätter and Lessing (*Ber.*, 1902, **35**, 2065), who also obtained a liquid by-product which they regarded as a liquid form of the solid ester, but which they could not obtain in the pure state. The pure liquid ethyl αδ-dibromoadipate has now been obtained, and is undoubtedly stereoisomeric with the solid form, since, on keeping the former, it is partly, but not entirely, converted into the latter.

When ethyl aδ-dibromoadipate is heated with an excess of monoethylaniline, a 62·5 per cent. yield of *ethyl 1-phenylpyrrolidine-2:5-dicarboxylate* (I) is obtained, together with a small quantity of *ethyl diethylanilinoadipate* (II):



(I.)

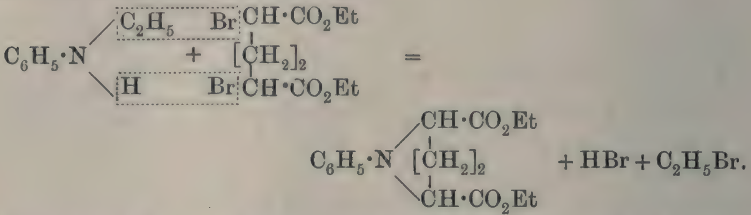


$$\begin{array}{c} C_6H_5\cdot N(C_2H_5)\cdot CH\cdot CO_2Et \\ | \\ [CH_2]_2 \\ | \\ C_6H_5\cdot N(C_2H_5)\cdot CH\cdot CO_2Et \end{array}$$

(II.)

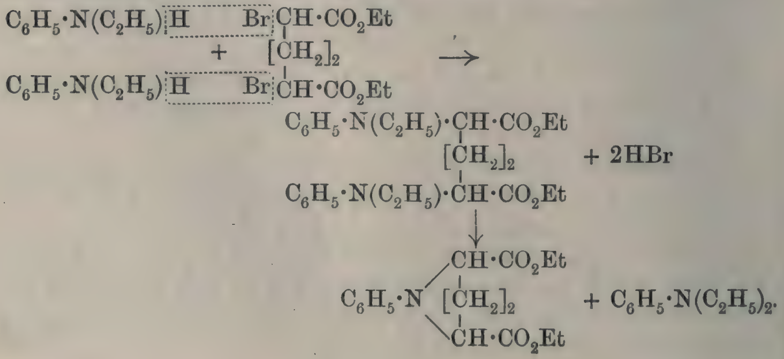
Hydrogen bromide is also eliminated, and combines with the excess of monoethylaniline to form the crystalline hydrobromide of this base.

The formation of the above pyrrolidine ester might result from a direct condensation of one molecule of monoethylaniline with one molecule of the ethyl dibromoadipate.



This is not the case, however, as no ethyl bromide could be detected at any stage of the reaction; moreover, the whole of the bromine is eliminated as hydrogen bromide, as was proved by the fact that the weight of monoethylaniline hydrobromide actually obtained accounted for 93 per cent. of the total bromine, whereas if the reaction had taken place according to the above equation, only half of the bromine would have been recovered in this form.

In view of this fact, and that ethyl aδ-diethylanilinoadipate was isolated from the products of the reaction, it is very highly probable that this latter substance is first formed, and that it loses diethylaniline with production of the pyrrolidine ester:



This ready formation of a ring compound from an open chain of six carbon atoms is no doubt due to the close proximity of the end carbon atoms, and also to the stability of five-membered ring compounds in general.

A reaction similar to the one described above enabled Willstätter and Lessing (*loc. cit.*) to prepare 1-methylpyrrolidine-2 : 5-dicarboxylic acid, but it appears that the formation of heterocyclic compounds from open-chain compounds and more particularly dicarboxylic acids has not been studied systematically, and this investigation is now being carried out.

EXPERIMENTAL.

The adipic acid used in this investigation was obtained by the oxidation of *cyclo*hexanol with concentrated nitric acid (Bouveault, *Bull. Soc. chim.*, 1908, [iv], **3**, 437); this method is much more rapid than that depending on the oxidation of *cyclo*hexanone with potassium permanganate, and the yield of adipic acid is 62 per cent. of that theoretically obtainable.

Fifty grams of adipic acid were converted into the dibromo-acid chloride by means of phosphorus pentachloride and bromine as described in a previous communication (Trans., 1908, **93**, 718). The resulting dibromo-acid chloride was gradually added to twice its volume of absolute alcohol, and the solution allowed to remain overnight, at the end of which time 35 grams of ethyl $\alpha\delta$-dibromoadipate had separated out. This, after recrystallisation from light petroleum, melted at 67°, a melting point which agrees with that found for this substance by Willstätter and Lessing (*loc. cit.*, p. 2067):

0·1772 gave 0·1864 AgBr. Br = 44·75.

$C_{10}H_{16}O_4Br_2$ requires Br = 44·44 per cent.

The alcoholic mother liquor was diluted with a large volume of water, extracted with ether, the ethereal solution washed, dried, evaporated, and the residue distilled under 33 mm. pressure, when the following fractions were obtained:

130—190°	5 grams
190—210	40 ,,
210—220°	25 grams

The last two fractions were redistilled together, when 57·4 grams of pure ester, boiling at 204—206°, were obtained. A portion collected at 204° was analysed:

0·2264 gave 0·2342 AgBr. Br = 44·02.

$C_{10}H_{16}O_4Br_2$ requires Br = 44·44 per cent.

The liquid form of ethyl $\alpha\delta$-dibromoadipate is a viscid, oily liquid, which, on keeping, is partly, but not wholly, converted into the solid form melting at 67°. The total yield of pure ester, both solid and liquid, from 50 grams of adipic acid amounted to 92·4 grams, which corresponds with 75·2 per cent. of the theoretical.

Methyl αδ-dibromoadipate was prepared in exactly the same way as the ethyl ester, methyl alcohol being used instead of ethyl alcohol. It is readily soluble in benzene, chloroform, acetone, ether, moderately so in alcohol, and sparingly so in light petroleum, from which it crystallises in long needles melting at 75—76°:

0·1844 gave 0·2108 AgBr. Br = 48·6.

$C_8H_{12}O_4Br_2$ requires Br = 48·2 per cent.

Action of Monoethylaniline on Ethyl αδ-Dibromoadipate.

Fifty grams of ethyl αδ-dibromoadipate and 70 grams of monoethylaniline were heated together in a flask attached to a reflux condenser and immersed in boiling water for thirteen and a-half hours; on cooling, a large quantity of a crystalline solid separated; a large quantity of ether was then added to the contents of the flask, which were then filtered, and the solid well washed with ether. The solid weighed 50 grams, and consisted of the hydrobromide of monoethylaniline, as was proved by crystallising it from a mixture of alcohol and ether, when it melted at 166°.

Bischoff (*Ber.*, 1897, **30**, 3178) gives 165—166° as the melting point of the pure substance.

The ethereal filtrate was evaporated, and the residue again heated in boiling water for twenty-eight and a-half hours. The product was then dissolved in dilute hydrochloric acid, the solution extracted with ether, the ethereal solution well washed with water, dried, evaporated, and the residue distilled under 35 mm. pressure:

224—240° ………	27 grams
240—260 ………	3 ,,
260—286°………	6·6 grams

The first fraction was redistilled under 30 mm. pressure, when 24 grams, distilling at 226—230°, were obtained. A portion boiling at 227—228° was analysed:

0·1560 gave 0·3762 CO_2 and 0·1052 H_2O. C = 65·77; H = 7·50.

0·1622 ,, 6·5 c.c. N_2 (moist) at 15° and 770 mm. N = 4·76.

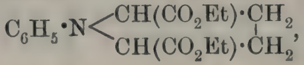
$C_{16}H_{21}O_4N$ requires C = 65·98; H = 7·22; N = 4·81 per cent.

A molecular-weight determination by the freezing-point method gave the following results:

0·6776 in 19·1388 naphthalene gave Δt − 0·87°; whence M.W. = 281.

$C_{16}H_{21}O_4N$ requires M.W. = 291.

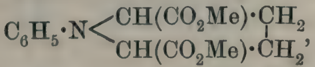
Ethyl 1-*phenylpyrrolidine*-2 : 5-*dicarboxylate*,



$$C_6H_5\cdot N<\begin{matrix}CH(CO_2Et)\cdot CH_2\\ \vert\\ CH(CO_2Et)\cdot CH_2\end{matrix},$$

is a pale yellow, oily liquid boiling at 227—228°/30 mm. It is insoluble in water, but dissolves readily in all the ordinary organic solvents and in concentrated aqueous hydrochloric acid. Its solution in chloroform readily absorbs bromine, with evolution of hydrogen bromide.

Methyl 1-*phenylpyrrolidine*-2 : 5-*dicarboxylate*,



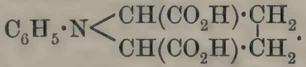
$$C_6H_5\cdot N\!<\!\begin{array}{l}CH(CO_2Me)\cdot CH_2\\ \qquad\qquad\quad\;\; | \\ CH(CO_2Me)\cdot CH_2\end{array},$$

was obtained by heating together methyl αδ-dibromoadipate (30 grams) and monoethylaniline (50 grams), and working up the product exactly as described for the preparation of the corresponding ethyl ester. The residue left after evaporation of the ethereal solution deposited a large amount of crystalline solid. This was separated and crystallised from light petroleum, when the methyl ester was obtained in stellar aggregates of needles which melted at 88°.

It is insoluble in water, alcohol or light petroleum in the cold, and readily dissolves in ether, chloroform, acetone or benzene, and in hot alcohol:

0·1682 gave 7·5 c.c. N_2 (moist) at 10° and 756 mm. N = 5·31.
$C_{14}H_{17}O_4N$ requires N = 5·32 per cent.

1-*Phenylpyrrolidine*-2 : 5-*dicarboxylic Acid*,



$$C_6H_5\cdot N\!<\!\begin{array}{l}CH(CO_2H)\cdot CH_2\\ \qquad\qquad\quad | \\ CH(CO_2H)\cdot CH_2\end{array}.$$

—Nine grams of ethyl 1-pyrrolidine-2:5-dicarboxylate were dissolved in a solution of 8·5 grams of potassium hydroxide in 80 c.c. of alcohol and 2 c.c. of water, contained in a flask attached to a reflux condenser, and the resulting solution boiled for nine hours. When cold, the solution was extracted once with ether in order to remove any unchanged ester, and then acidified with dilute sulphuric acid, when the acid was precipitated in a crystalline state, and, when dry, weighed 6·5 grams. It was recrystallised from a mixture of acetone and light petroleum and analysed:

0·1574 gave 0·3516 CO_2 and 0·0798 H_2O. C = 60·92 ; H = 5·63.
0·1674 ,, 8·7 c.c. N_2 (moist) at 14° and 775 mm. N = 6·23.
$C_{12}H_{13}O_4N$ requires C = 61·27 ; H = 5·53 ; N = 5·96 per cent.

1-*Phenylpyrrolidine*-2 : 5-*dicarboxylic acid* crystallises from a mixture of acetone and light petroleum in well-defined, oblong plates, and decomposes with evolution of gas at 252°. It dissolves readily in cold alcohol or hot acetone, is insoluble in benzene, light petroleum or chloroform, sparingly soluble in cold ether or water, and moderately so in boiling water or concentrated hydrochloric acid. It decolorises an acid or alkaline solution of potassium permanganate, and its aqueous solution gives a flocculent precipitate with an aqueous solution of bromine.

The vapour produced by heating the acid alone, or preferably with soda-lime, imparts a red colour to a pine shaving which has been previously moistened with hydrochloric acid.

The molecular weight was determined by dissolving the acid in alcohol and titrating with *N*/10 sodium hydroxide, using phenolphthalein as indicator:

0·2122 required 17·7 c.c. *N*/10 NaOH. M.W. = 239·6.

A dibasic acid, $C_{12}H_{13}O_4N$, requires M.W. = 235.

The *silver* salt was obtained as a white precipitate by adding an ice-cold solution of the ammonium salt of the acid to an ice-cold solution of silver nitrate, the operation being carried out in the dark. If the precipitation is carried out in warm solutions the salt immediately decomposes and black, metallic silver is precipitated:

0·2540 gave 0·1214 Ag. Ag = 47·80.

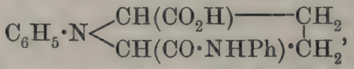
$C_{12}H_{11}O_4NAg_2$ requires Ag = 48·10 per cent.

The *barium* salt was prepared by carefully neutralising the acid with an aqueous solution of barium hydroxide. The solution was filtered and, after concentration to a small bulk, alcohol was added, when, on cooling, the barium salt separated in stout needles, which were collected and dried in the air for several days. The salt is readily soluble in water, and is insoluble in absolute alcohol:

0·2062 gave 0·0930 $BaSO_4$. Ba = 26·52.

0·7506 lost 0·2042 at 135°. H_2O = 27·20.

$C_{12}H_{11}O_4NBa,8H_2O$ requires Ba = 26·65; H_2O = 28·0 per cent.

The monoanilide, 
$C_6H_5\cdot N{<}\begin{array}{l}CH(CO_2H)\text{——}CH_2\\ CH(CO\cdot NHPh)\cdot CH_2\end{array}$, was prepared by boiling the acid with an excess of recently-distilled aniline for six and a-half hours. The resulting product was treated with dilute hydrochloric acid, extracted with ether, the ethereal solution washed, dried, evaporated, and the residue crystallised from a mixture of chloroform and benzene, when the substance was obtained in small needles which decompose at 184°. It readily dissolves in an aqueous solution of potassium hydroxide, alcohol or acetone, and is but slightly soluble in benzene, light petroleum, chloroform or cold water. Its solution in hot water has a well marked acid reaction:

0·1006 gave 7·7 c.c. N_2 (moist) at 17° and 749 mm. N = 8·76.

$C_{18}H_{18}O_3N_2$ requires N = 9·03 per cent.

Ethyl aδ-Diethylanilinoadipate,

$CO_2Et\cdot CH(NEtPh)\cdot CH_2\cdot CH_2\cdot CH(NEtPh)\cdot CO_2Et$.

—The fraction boiling at 260—286° (see p. 276) was kept for several weeks, at the end of which time it had partly solidified. It was then well pressed on porous plate, and the solid thus obtained crystallised from dilute alcohol:

0·1588 gave 0·4110 CO_2 and 0·1190 H_2O. C = 70·59; H = 8·32.
0·1766 ,, 9·7 c.c. N_2 (moist) at 12·5° and 758 mm. N = 6·49.
$C_{26}H_{36}O_4N_2$ requires C = 70·90; H = 8·18; N = 6·36 per cent.

Ethyl αδ-diethylanilinoadipate crystallises from alcohol in stout prisms melting at 88—90°. It is insoluble in water or light petroleum, but dissolves readily in ether, benzene, chloroform, acetone or dilute hydrochloric acid.

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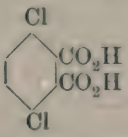
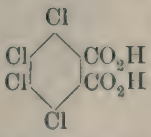
XXXV.—*Derivatives of Naphthacenequinone. Part III.*

By Dorothy Harrop, Roland Victor Norris, and
Charles Weizmann.

In the last communication on this subject (Trans., 1907, **91**, 1588), certain derivatives of naphthacenequinone were described which had been obtained from the products of condensation of the two nitrophthalic acids with α-naphthol. The yields obtained by these reactions, however, were so unsatisfactory that a new method was sought to obtain derivatives of naphthacenequinone containing substituent groups in the benzene nucleus, the study of which has always appeared to be of considerable interest. Having this object in view, it seemed to us that the most suitable derivatives of phthalic acid to employ as starting material were di- and tetra-chlorophthalic acids, both of which, being technical products, are easily accessible and comparatively cheap.

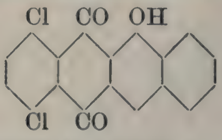
Finding that the technical dichlorophthalic acid consisted mainly of the 3:6-dichloro-derivative, the suitability of these two acids became still more obvious, because, as will be seen from their formulæ,





,

each acid contains two chlorine atoms in positions adjacent to the carboxyl groups, and would therefore, by condensation with α-naphthol, give rise to chlorinated hydroxynaphthacenequinones,



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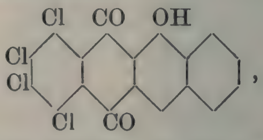
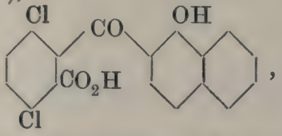


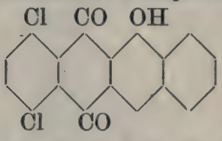
containing two chlorine atoms in adjacent positions to the carbonyl groups. It was to be expected therefore that these chlorine atoms would be easily replaceable by other groups, and that such substitution products would be the means of preparing a great variety of naphthacenequinone derivatives. Our anticipations in this respect have, to a great extent, been realised, but the yields obtained in the primary condensation with α-naphthol leave much to be desired.

The condensation of 3 : 6-dichlorophthalic anhydride with α-naphthol in presence of boric acid yields 3 : 6-*dichloro*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic acid* (m. p. 187°),

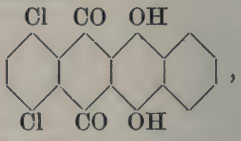


which on bromination is converted into a monobromo-derivative, presumably 3 : 6-*dichloro*-4′-*bromo*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic acid* (m. p. 221°).

These two acids on treatment with sulphuric and boric acids yield respectively 7 : 10-*dichloro*-1-*hydroxynaphthacenequinone* and 7 : 10-*dichloro*-1 : 6-*dihydroxynaphthacenequinone*,

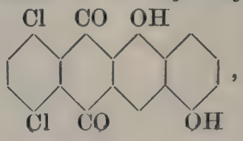


and



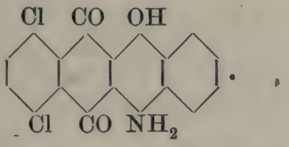
the production of the latter being due to the replacement of the bromine by the hydroxyl group, which is assumed to be in the para-position with respect to the first hydroxyl group (Orchardson and Weizmann, Trans., 1906, 89, 117). On sulphonation, the dihydroxy-compound yields a mordant dye similar to quinizarin.

By employing 1 : 5-dihydroxynaphthalene in place of α-naphthol in the reactions just described, we succeeded in preparing an isomeric quinone, namely, 7 : 10-*dichloro*-1 : 5-*dihydroxynaphthacenequinone*,



although we were unable to isolate the intermediate naphthoylbenzoic acid in a state sufficiently pure for analysis.

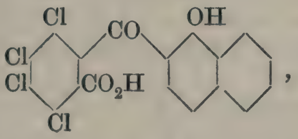
3 : 6-Dichloro-1′-hydroxy-2-β-naphthoylbenzoic acid produces with diazobenzene chloride in alkaline solution an azo-dye, which on reduction yields 3 : 6-*dichloro*-4′-*amino*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic acid*, and this condenses in sulphuric acid solution to the corresponding 7 : 10-*dichloro*-6-*amino*-1-*hydroxynaphthacenequinone*,



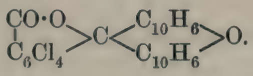
As the chlorine atoms in 7 : 10-dichloro-1-hydroxynaphthacenequinone are adjacent to the carbonyl groups, it was anticipated that one or both would be easily removed by primary amines, and this was proved to be the case, aniline and *p*-toluidine yielding respectively 7(10)-*chloro*-10(7)-*anilino*-1-*hydroxynaphthacenequinone* and 7(10)-*chloro*-10(7)-p-*toluidino*-1-*hydroxynaphthacenequinone*, which are crystalline substances giving rise on sulphonation to greenish-black dyes.

In the case of 7 : 10-dichloro-1 : 5-dihydroxynaphthacenequinone, treatment with aniline appeared to give the dianilino-derivative, but the product could not be obtained entirely free from chlorine.

Tetrachlorophthalic acid when condensed with α-naphthol furnishes the corresponding 3 : 4 : 5 : 6-*tetrachloro*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic* acid (m. p. 212°),

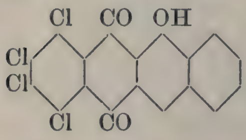


but the yield is somewhat small, on account of the reaction leading also to the formation of the fluoran derivative,



$$\begin{matrix}CO\cdot O\\ | \\ C_6Cl_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}\!>\!O.$$

However, it was found that a further quantity of the same acid could be obtained by fusing the fluoran with sodium hydroxide at high temperatures, one molecule of naphthol being eliminated in the process, but curiously enough the chlorine atoms remain intact. The acid on being heated with bromine in acid solution yields a *monobromo*-derivative (m. p. 216°). The original acid and its mono-bromo-derivative when heated with sulphuric and boric acids yield respectively the corresponding 7 : 8 : 9 : 10-*tetrachloro*-1-*hydroxynaphthacenequinone* and 7 : 8 : 9 : 10-*tetrachloro*-1 : 6-*dihydroxynaphthacenequinone* :



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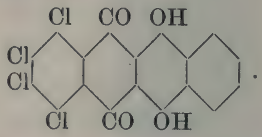
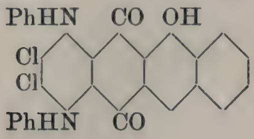


Both these quinones when boiled with aniline in the presence of boric acid lose two atoms of chlorine, yielding presumably 8 : 9-*dichloro*-7 : 10-*dianilino*-1-*hydroxynaphthacenequinone* and 8 : 9-*dichloro*-7 : 10-*dianilino*-1 : 6-*dihydroxynaphthacenequinone* respectively :



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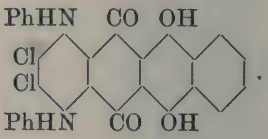


EXPERIMENTAL.

The 3 : 6-dichlorophthalic acid employed in this research was obtained by crystallising technical dichlorophthalic acid from glacial acetic acid repeatedly until a product was obtained melting at 185°. Unless a pure acid is used, the yields obtained in the subsequent reactions are most unsatisfactory. The acid is then distilled under diminished pressure, and thus converted into its anhydride.

3 : 6-*Dichloro*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic Acid.*—This acid is obtained by heating a mixture of 3 : 6-dichlorophthalic anhydride (108 grams), *α*-naphthol (72 grams), and boric acid (350 grams) to 180—190° for three hours. The molten product is poured into water and extracted with much warm water to remove boric acid, and the semi-solid residue is distilled in a current of superheated steam to remove unchanged *α*-naphthol ; the residue is then boiled with sodium carbonate and animal charcoal, the alkaline extract filtered and acidified with hydrochloric acid, and the voluminous precipitate collected, dried, and purified by crystallisation from acetic acid :

0·2796 gave 0·6080 CO_2 and 0·0751 H_2O. C = 59·3 ; H = 2·98.
0·1067 „ 0·0815 AgCl. Cl = 18·9.
$C_{18}H_{10}O_4Cl_2$ requires C = 59·8 ; H = 2·7 ; Cl = 19·5 per cent.

3 : 6-*Dichloro*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic acid* crystallises from acetic acid in yellow needles melting at 187°. It is readily soluble in alcohol, but sparingly so in benzene, and dissolves in sodium carbonate, forming a deep yellow solution.

When treated in carbon disulphide suspension with bromine in the cold for twenty-four hours, and afterwards on the water-bath for three hours, it yields 3 : 6-*dichloro*-4′-*bromo*-1′-*hydroxy*-2-β-*naphthoylbenzoic acid*, which, after removing the carbon disulphide by distillation, washing the residue with sodium hydrogen sulphite, then with water, and crystallising from acetic acid, is obtained in yellow needles melting and decomposing at 221°. This bromo-acid is soluble in alkalis with a deep yellow colour; it is sparingly soluble in benzene, but readily so in acetic acid:

0·2930 gave 0·5219 CO_2 and 0·0618 H_2O. C = 48·56; H = 2·30.
0·1832 „ 0·1929 AgCl + AgBr. Cl + Br = 34·9.
$C_{18}H_9O_4Cl_2Br$ requires C = 49·1; H = 2·04; Cl + Br = 34·3 per cent.

7 : 10-*Dichloro*-1-*hydroxynaphthacenequinone*.—This substance is prepared by heating a mixture of 3 : 6-dichloro-1′-hydroxy-2-β-naphthoylbenzoic acid (10 grams), boric acid (10 grams), and fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) (100 grams) to 160° for fifteen minutes. The product is cooled, poured into ice-water, boiled, and filtered; the reddish-brown precipitate is then washed with dilute ammonia, dried, and purified by crystallisation from nitrobenzene:

0·1059 gave 0·2414 CO_2 and 0·0220 H_2O. C = 62·16; H = 2·11.
0·1135 „ 0·0922 AgCl. Cl = 20·1.
$C_{18}H_8O_3Cl_2$ requires C = 62·99; H = 2·33; Cl = 20·6 per cent.

It is sparingly soluble in alcohol or benzene. Its solution in concentrated sulphuric acid is reddish-blue, and becomes greener on the addition of fuming sulphuric acid. On warming with the latter reagent it is sulphonated.

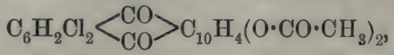
7 : 10-*Dichloro*-1 : 6-*dihydroxynaphthacenequinone*.—This quinone is prepared in the same manner as the preceding one, by heating 3 : 6-dichloro-4′-bromo-1′-hydroxy-2-β-naphthoylbenzoic acid with boric acid and fuming sulphuric acid at 160° until the evolution of hydrogen bromide and bromine has ceased. The product is purified by crystallisation from nitrobenzene, from which it separates in brownish-red needles:

0·1126 gave 0·2470 CO_2 and 0·0230 H_2O. C = 59·8; H = 2·3.
0·16295 „ 0·1285 AgCl. Cl = 19·4.
$C_{18}H_8O_4Cl_2$ requires C = 60·1; H = 2·2; Cl = 19·8 per cent.

7 : 10-*Dichloro*-1 : 6-*dihydroxynaphthacenequinone* dissolves in concentrated sulphuric acid, forming a reddish-violet solution which, on the addition of boric acid and warming, exhibits a strong, yellow fluorescence.

When heated with fuming sulphuric acid to 160° for an hour, it yields a sulphonic acid, which is soluble in water and is a mordant dyestuff similar to quinizarin.

7 : 10-*Dichloro*-1 : 6-*diacetoxynaphthacenequinone*,

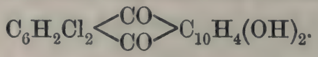


$$\mathrm{C_6H_2Cl_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{C_{10}H_4(O\cdot CO\cdot CH_3)_2},$$

is produced when the foregoing quinone (2 grams) is boiled with acetic anhydride (40 grams) in presence of a little zinc chloride for ten minutes. The solution, which changes from red to a brownish-yellow, is filtered hot, the filtrate boiled with water, and the crude acetyl compound which separates is collected, dried, and recrystallised from xylene, from which it is obtained in yellow crystals melting at 265°. It dissolves in concentrated sulphuric acid to a violet-red solution, and is readily hydrolysed on boiling with sodium hydroxide:

0·1013 gave 0·2202 CO_2 and 0·0265 H_2O. C = 59·39; H = 2·91.
$C_{22}H_{12}O_6Cl_2$ requires C = 59·6; H = 2·7 per cent.

1 : 5-*Dihydroxy*-7 : 10-*dichloronaphthacenequinone*,



$$\mathrm{C_6H_2Cl_2}<\genfrac{}{}{0pt}{}{\mathrm{CO}}{\mathrm{CO}}>\mathrm{C_{10}H_4(OH)_2}.$$

—When 1 : 5-dihydroxynaphthalene (80 grams) is condensed with 3 : 6-dichlorophthalic anhydride (108 grams) in presence of boric acid (350 grams) by the method already given, the corresponding intermediate naphthoylbenzoic acid is obtained, but its purification was found to be attended with such difficulty that it was abandoned, and the crude acid was converted directly into the corresponding quinone by heating with boric acid and fuming sulphuric acid (containing 20 per cent. of sulphur trioxide). The product is isolated as usual, and purified by crystallisation from nitrobenzene:

0·1133 gave 0·2503 CO_2 and 0·02393 H_2O. C = 60·26; H = 2·32.
0·1487 „ 0·1176 AgCl. Cl = 19·41.
$C_{18}H_8O_4Cl_2$ requires C = 60·1; H = 2·2; Cl = 19·75 per cent.

1 : 5 - *Dihydroxy* - 7 : 10 - *dichloronaphthacenequinone* forms red needles with a metallic lustre. It dissolves in concentrated sulphuric acid, producing a bluish-green solution, which, on the addition of boric acid and warming, becomes bluer. It is soluble in dilute aqueous sodium hydroxide with a violet-blue colour, and is sparingly soluble in alcohol or benzene, more readily so in xylene.

7 : 10-*Dichloro*-6-*amino*-1-*hydroxynaphthacenequinone*.—This derivative is most advantageously prepared by the following method: Pure 3 : 6-dichloro-1′-hydroxy-2-β-naphthoylbenzoic acid (20 grams) is dissolved in dilute aqueous potassium hydroxide (200 c.c. of a 5 per cent. solution) and treated with a solution of diazobenzene chloride (from 5·2 grams of aniline) in the cold. The precipitated azo-compound is collected, dissolved in warm sodium carbonate, and treated with a solution of sodium hyposulphite until the red colour of the azo-compound disappears. On acidifying with hydrochloric acid,

the amino-acid is precipitated in yellow crystals; these are collected, dried, and, without further purification, are mixed with boric and fuming sulphuric acids (containing 20 per cent. of sulphur trioxide) and heated to 160°. The quinone, after being isolated and purified in the usual way, is obtained in minute, black needles with a green metallic lustre:

0·1176 gave 0·2611 CO_2 and 0·0294 H_2O. $C = 60·55$; $H = 2·77$.
0·1955 „ 6·85 c.c. N_2 at 18° and 756 mm. $N = 4·02$.
0·1975 „ 0·1578 AgCl. $Cl = 19·62$.
$C_{18}H_9O_3NCl_2$ requires $C = 60·35$; $H = 2·51$; $N = 3·91$; $Cl = 19·81$ per cent.

7 : 10 - *Dichloro*-6-*amino*-1-*hydroxynaphthacenequinone* dissolves in boiling alcohol with a magenta-red colour, and in alcoholic potash with a blue colour. With aqueous potassium hydroxide it forms an insoluble blue salt. Its solution in concentrated sulphuric acid is purple and slightly fluorescent, and becomes more so on the addition of boric acid.

7(10)-*Chloro*-10(7)-*anilino*-1-*hydroxynaphthacenequinone*.—This substance is prepared by adding 7 : 10-dichloro-1-hydroxynaphthacenequinone (10 grams) to aniline (100 grams), and boiling the mixture in a reflux apparatus until the original red colour of the solution changes to blue. The solution, on cooling, deposits black crystals, which are collected and purified by crystallisation from xylene or nitrobenzene:

0·1355 gave 0·3567 CO_2 and 0·0437 H_2O; $C = 71·81$; $H = 3·57$.
0·1850 „ 5·4 c.c. N_2 at 18° and 757 mm. $N = 3·28$.
0·1865 „ 0·0644 AgCl. $Cl = 8·54$.
$C_{24}H_{14}O_3NCl$ requires $C = 72·09$; $H = 3·50$; $N = 3·50$; $Cl = 8·87$ per cent.

In a similar manner from *p*-toluidine is prepared 7(10)-*chloro*-10(7)-p-*toluidino*-1-*hydroxynaphthacenequinone*:

0·1241 gave 0·3290 CO_2 and 0·0452 H_2O. $C = 72·31$; $H = 4·05$.
0·1338 „ 4·4 c.c. N_2 at 21° and 758 mm. $N = 3·7$.
0·1834 „ 0·0624 AgCl. $Cl = 8·41$.
$C_{25}H_{16}O_3NCl$ requires $C = 72·56$; $H = 3·86$; $N = 3·3$; $Cl = 8·57$ per cent.

Both the anilino- and the *p*-toluidino-compounds crystallise in brownish-black needles possessing a metallic lustre. They are soluble in hot acetic acid and xylene, and dissolve in ordinary concentrated sulphuric acid with a violet colour, which changes to dark green on the addition of fuming sulphuric acid. When heated with fuming sulphuric acid, they are sulphonated with the formation of greenish-black dyes.

7 : 10-*Dianilino*-1 : 5-*dihydroxynaphthacenequinone*.—As stated in the introduction, the action of boiling aniline on 1 : 5-dihydroxy-7 : 10-naphthacenequinone results in the formation of a dianilino-derivative. The substance was obtained in black needles with a green lustre. It is soluble in hot xylene or nitrobenzene, and

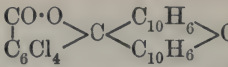
sparingly so in benzene, alcohol or acetic acid. Its solution in concentrated sulphuric acid is blue. The results of the analyses of this substance indicated the constitution assigned to it, but it was not found possible to obtain it perfectly free from chlorine.

3 : 4 : 5 : 6-*Tetrachloro*-1′-*hydroxy*-2-β-*naphthoylbenzoic Acid.*—Tetrachlorophthalic anhydride (100 grams), α-naphthol (50 grams), and boric acid (300 grams) are intimately mixed and rapidly heated (on an oil-bath heated to 250°) until the fusion becomes quite homogeneous. It is then poured into water, extracted repeatedly with hot water until free from boric acid, and the residue is digested with dilute aqueous sodium hydroxide, which removes the acid from the insoluble fluoran derivative. On acidifying the alkaline solution, the acid is obtained as a pale yellow precipitate, which, when dried and crystallised from xylene, separates in orange needles melting at 212°:

0·1004 gave 0·1846 CO_2 and 0·0194 H_2O. C = 50·16; H = 2·15.
0·1778 „ 0·2391 AgCl. Cl = 33·2.
$C_{18}H_8O_4Cl_4$ requires C = 50·25; H = 1·9; Cl = 33·0 per cent.

The analysis of this acid is extraordinarily difficult, and good results can only be obtained when the substance is intimately mixed with lead chromate before its introduction into the combustion tube.

3 : 4 : 5 : 6-*Tetrachloro*-1′-*hydroxy*-2-β-*naphthoylbenzoic acid* is readily soluble in alcohol, acetic acid or xylene, but only sparingly so in ether. When added to sodium hydroxide or sodium carbonate solution, it yields an extremely voluminous, pale yellow *sodium* salt, which is sparingly soluble in water.

Tetrachloro-α-naphthafluoran,  $\begin{matrix}CO\cdot O\\ |\\ C_6Cl_4\end{matrix}>C<\begin{matrix}C_{10}H_6\\ C_{10}H_6\end{matrix}>O$.—This substance is formed in the preparation of the above-mentioned acid, and remains as an insoluble powder after the extraction of the acid with alkalis. It is best obtained pure by recrystallisation from glacial acetic acid, in which solvent, however, it is very sparingly soluble:

0·1543 gave 0·3543 CO_2 and 0·0324 H_2O. C = 62·62; H = 2·33.
0·1887 „ 0·1999 AgCl. Cl = 26·2.
$C_{28}H_{12}O_3Cl_4$ requires C = 62·47; H = 2·23; Cl = 26·36 per cent.

Tetrachloro-α-naphthafluoran forms grey, feathery crystals, which do not melt below 300°. It is soluble in boiling xylene or nitrobenzene, but does not crystallise well from these solvents. It dissolves in concentrated sulphuric acid, giving a brown, strongly fluorescent solution. It is quite insoluble in aqueous sodium hydroxide, but when fused with the alkali it loses one molecule of naphthol and yields the sodium salt of 3 : 4 : 5 : 6-tetrachloro-1′-hydroxy-2-β-naphthoylbenzoic acid. Small quantities of this acid may be obtained in this way. The operation is carried out as follows: The crude fluoran is mixed with six times its weight of powdered sodium hydroxide and a small quantity of potassium hydroxide, and, after the addition of a little water, the mixture, while being constantly stirred, is heated to 180° for about half an hour and finally raised to 250° for a few minutes. The greenish-brown product is then cooled, extracted with hot water, and the acid precipitated by the addition of hydrochloric acid.

3 : 4 : 5 : 6-*Tetrachloro*-4′-*bromo*-1′-*hydroxy*-2-*β*-*naphthoylbenzoic acid* is produced by gently boiling an acetic acid solution of 3 : 4 : 5 : 6-tetrachloro-1′-hydroxy-2-β-naphthoylbenzoic acid (50 grams) with bromine (20 grams) for thirty-six hours. The product is poured into water, and the precipitate is collected, washed with sodium hydrogen sulphite solution, and crystallised from xylene :

0·1536 gave 0·24035 CO_2 and 0·0229 H_2O. C = 42·67 ; H = 1·6.
0·1662 ,, 0·2078 AgCl + AgBr. Cl + Br = 43·5
$C_{18}H_7O_4Cl_4Br$ requires C = 42·47 ; H = 1·38 ; Cl + Br = 43·6 per cent.

This acid is a pale yellowish-green, crystalline powder melting at 216°. It dissolves readily in alcohol or acetic acid, but sparingly so in xylene or nitrobenzene. Its *sodium* salt is sparingly soluble in water, and separates as a flocculent precipitate when the acid is mixed with sodium carbonate solution.

7 : 8 : 9 : 10-*Tetrachloro*-1-*hydroxynaphthacenequinone*.—This quinone results from the action of boric and fuming sulphuric acids on 3 : 4 : 5 : 6-tetrachloro-1′-hydroxy-2-β-naphthoylbenzoic acid. The method of preparation is similar to that described in the earlier part of this paper. It is necessary to use strongly fuming acid (containing 50—70 per cent. of sulphur trioxide), and at the same time to be careful to avoid sulphonation, the temperature not being allowed to exceed 130°. The quinone is purified by crystallisation from acetic acid :

0·1026 gave 0·1967 CO_2 and 0·0152 H_2O. C = 52·29 ; H = 1·64.
0·1551 ,, 0·21514 AgCl. Cl = 34·30.
$C_{18}H_6O_3Cl_4$ requires C = 52·45 ; H = 1·45 ; Cl = 34·43 per cent.

7 : 8 : 9 : 10-*Tetrachloro*-1-*hydroxynaphthacenequinone* forms a brick-red, crystalline powder, sparingly soluble in acetic acid, alcohol or xylene, more readily so in boiling nitrobenzene. With concentrated sulphuric acid, it yields a deep red solution, which becomes violet on the addition of fuming sulphuric acid. When warmed with concentrated sulphuric and boric acids, the quinone yields a red solution possessing a yellow fluorescence.

7 : 8 : 9 : 10-*Tetrachloro*-1 : 6-*dihydroxynaphthacenequinone* is prepared by heating 3 : 4 : 5 : 6-tetrachloro-4′-bromo-1′-hydroxy-2-β-naphthoylbenzoic acid with boric acid and fuming sulphuric acid (containing 10 per cent. of sulphur trioxide) at 180° until the evolution of

hydrogen bromide and bromine has ceased. The quinone is isolated in the usual way, and crystallises from nitrobenzene in brown, lustrous crystals :

0·1064 gave 0·1952 CO_2 and 0·0155 H_2O. C = 50·01 ; H = 1·61.
0·1132 „ 0·1512 AgCl. Cl = 33·04.
$C_{18}H_6O_4Cl_4$ requires C = 50·49 ; H = 1·40 ; Cl = 33·14 per cent.

It is very sparingly soluble in alcohol or acetic acid, more readily so in xylene or nitrobenzene. When dissolved in concentrated sulphuric acid, it exhibits a beautiful red fluorescence. With alkalis, it yields bluish-purple, insoluble salts.

8 : 9-*Dichloro*-7 : 10-*dianilino*-1-*hydroxynaphthacenequinone* results when 7 : 8 : 9 : 10-tetrachloro-1-hydroxynaphthacenequinone, mixed with a little boric acid, is boiled with aniline for twelve hours. The olive-green solution is poured into a mixture of alcohol and hydrochloric acid, the precipitate collected, washed free from aniline hydrochloride, and crystallised from nitrobenzene, from which it separates as a dark green powder. It is readily soluble in hot xylene :

0·1130 gave 0·2826 CO_2 and 0·0372 H_2O. C = 68·27 ; H = 3·65.
0·1265 „ 6·0 c.c. N_2 at 20° and 764 mm. N = 5·45.
0·1828 „ 0·09847 AgCl. Cl = 13·32.
$C_{30}H_{18}O_3Cl_2N_2$ requires C = 68·58 ; H = 3·41 ; N = 5·33 ; Cl = 13·50 per cent.

8 : 9-*Dichloro*-7 : 10-*dianilino*-1 : 6-*dihydroxynaphthacenequinone* is obtained in a similar manner by boiling 7 : 8 : 9 : 10-tetrachloro-1 : 6-dihydroxynaphthacenequinone with aniline in the presence of a little boric acid. It is a dark green, crystalline substance, insoluble in alcohol or ether, but moderately so in xylene or nitrobenzene :

0·1541 gave 0·3744 CO_2 and 0·0485 H_2O. C = 66·26 ; H = 3·5.
0·1121 „ 4·9 c.c. N_2 at 20° and 762 mm. N = 5·01.
0·1737 „ 0·0935 AgCl. Cl = 13·31.
$C_{30}H_{18}O_4Cl_2N_2$ requires C = 66·55 ; H = 3·32 ; N = 5·17 ; Cl = 13·1 per cent.

THE UNIVERSITY,
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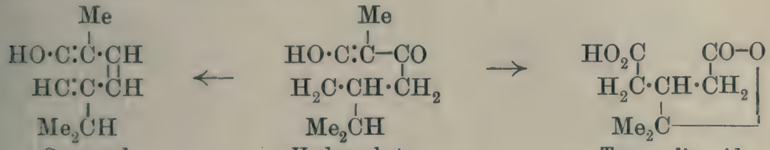
XXXVI.—*Contributions to the Chemistry of the Terpenes. Part IV. The Oxidation of Pinene with Mercuric Acetate.*

By GEORGE GERALD HENDERSON and JAMES WATSON AGNEW.

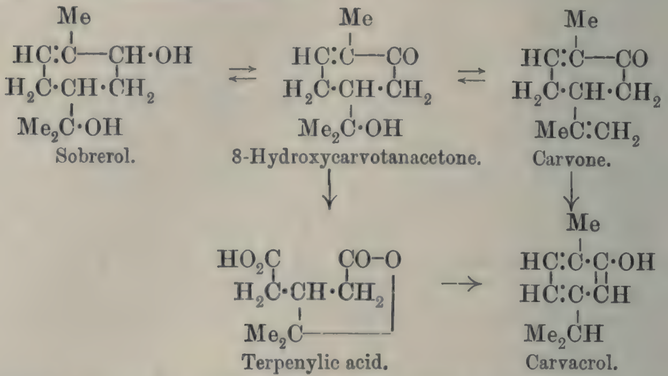
BY the oxidation of pinene with an aqueous solution of mercuric acetate, Balbiano (*Ber.*, 1902, **35**, 2994; 1903, **36**, 3575) obtained a hydroxyketone of the formula $C_{10}H_{15}O{\cdot}OH$. He found that this compound was almost completely converted into carvacrol when warmed with dilute sulphuric acid, and that it yielded terpenylic acid when oxidised with an acidified solution of potassium permanganate; he therefore concluded that it was 6-hydroxycarvotanacetone (6-hydroxy-Δ^6-menthen-2-one):



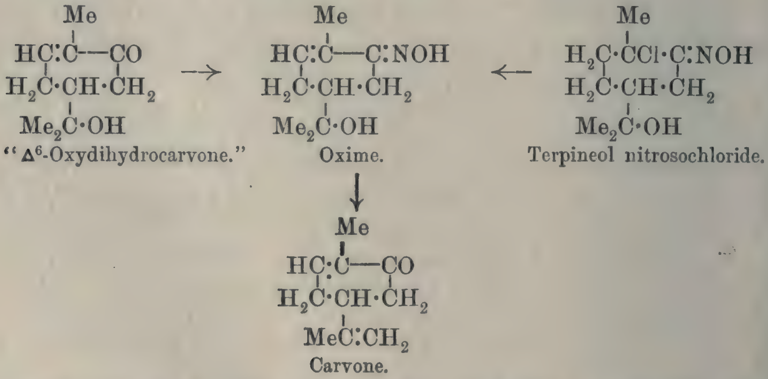
Carvacrol. Hydroxyketone. Terpenylic acid.

In the hope of obtaining an isomeride of sobrerol, he attempted to reduce the hydroxyketone under varying conditions, but without result.

Through the introduction of several modifications of the process described by Balbiano, we have found that when pinene is oxidised with aqueous mercuric acetate at the ordinary temperature, the first product of the reaction is inactive sobrerol, $C_{10}H_{16}(OH)_2$, and that the sobrerol is converted into the hydroxyketone by the further action of the same reagent. In its boiling point (154°/10 mm.) and other physical properties the hydroxyketone closely resembles 8-hydroxycarvotanacetone, which has already been prepared from carvone by agitation with 40 per cent. sulphuric acid (Rupe and Schlochoff, *Ber.*, 1905, **38**, 1719), and its semicarbazone melts at the same temperature (176°) as the semicarbazone prepared from 8-hydroxycarvotanacetone. Moreover, through the action of anhydrous oxalic acid, the hydroxyketone is converted by the elimination of one molecule of water into a mixture of carvone and carvacrol, the latter compound, no doubt, having been produced from the carvone by heating with the oxalic acid. Finally, the hydroxyketone is reconverted into sobrerol by reduction with sodium in moist ether; it is converted into carvacrol by the action of aqueous hydriodic acid, and, on oxidation, yields terpenylic acid. All these considerations lead to the conclusion that the hydroxyketone is 8-hydroxycarvotanacetone (8-hydroxy-Δ^6-menthen-2-one), and not the 6-hydroxy-derivative as supposed by Balbiano. The relationship between the compounds is shown in the following scheme:



Wallach (*Annalen*, 1896, **291**, 342) found that inactive sobrerol (pinol hydrate), on oxidation with chromium trioxide dissolved in acetic acid, yielded a viscous liquid to which he assigned the formula $C_{10}H_{15}(OH)O$ on the basis of his analyses of its semicarbazone (m. p. 174°) and oxime (m. p. 134°). The oxime was proved to be identical with the compound obtained by the elimination of hydrogen chloride from terpineol nitrosochloride, and, in particular, was found to yield carvone when warmed with dilute sulphuric acid. For these reasons Wallach concluded that the compound $C_{10}H_{15}O\cdot OH$ is a "Δ^6-oxydihydrocarvone," with the formula given below:



There can be no doubt that this hydroxyketone is identical with the compound prepared by Balbiano and by ourselves, and Wallach's own work led him to assign to it the same constitution as we have done.

So far as we are aware, sobrerol has not hitherto been prepared directly from pinene except by the method, based on Sobrero's discovery and applied by Armstrong and Pope (Trans., 1891, **59**, 315), of oxidising the hydrocarbon by means of moist oxygen in bright sunlight, although, of course, it can be obtained by the hydration of pinol, which, according to Wallach and Otto (*Annalen*, 1889, **253**, 249), is formed as a by-product in the preparation of pinene nitrosochloride. By the method, which is described below, of oxidising pinene with aqueous mercuric acetate, sobrerol is obtained without difficulty and in fairly satisfactory quantity. We have also found that it can be prepared by the action of mercuric oxide on a cold solution of pinene in acetic acid, but in this case the yield is poor.

EXPERIMENTAL.

Preparation of Sobrerol from Pinene.—Fifty grams of pinene were added to a solution of 350 grams of mercuric acetate in 1500 c.c. of water, and the mixture was shaken continuously at the ordinary temperature. The reaction began at once, mercurous acetate, and finally mercury, being precipitated and the pinene gradually disappearing. After ten days, the solution was neutralised with sodium carbonate and filtered, and the filtrate was agitated repeatedly with chloroform. The chloroform solution was washed with water and dried with anhydrous potassium carbonate, and the chloroform was then distilled off, leaving an oily residue which, on treatment with a few drops of benzene, became for the most part crystalline. A small quantity of the oily hydroxyketone, which was also present, was drained off, and the solid was purified by crystallisation from benzene.

The lustrous, colourless crystals thus obtained melted at 131°, the same temperature as inactive * sobrerol, $C_{10}H_{16}(OH)_2$. A small quantity of the crystals was dissolved in dry chloroform, and the calculated amount (one molecular proportion) of dry bromine was added. A colourless, crystalline additive product separated, and was found to have the same melting point as sobrerol dibromide,

$$C_{10}H_{16}Br_2(OH)_2,$$

namely, 131—132°. Another quantity of the crystals was warmed with dilute sulphuric acid, and the oily product was separated by distillation in a current of steam, extracted with ether, and, after removal of the ether, distilled under the ordinary pressure. The oily liquid had the same odour and the same boiling point (183—184°) as pinol, $C_{10}H_{16}O$, and, when treated with one molecular proportion of bromine in solution in dry chloroform, was converted into a beautifully crystalline additive product, which was found to melt at 94°, the same temperature as pinol dibromide, $C_{10}H_{16}Br_2O$. In all these respects the behaviour of the crystalline compound obtained by the oxidation of pinene in the manner just described was identical with that of inactive sobrerol, and therefore there can be no doubt as to its constitution.

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* The pinene used in the experiment was only feebly dextrorotatory, $[\alpha]_D^{20} = 5{\cdot}8°$.

Although the yield of sobrerol obtained from pinene by this method is fairly satisfactory, a number of modifications in the process were tried in the hope of improving it, but these were all more or less unsuccessful. We found, however, that sobrerol can also be obtained by the action of mercuric oxide at the ordinary temperature on a solution of pinene in glacial acetic acid. Yellow mercuric oxide was added in small portions to the solution (the quantities taken corresponding with those used in the first method), and, after each addition, the mixture was shaken until action had apparently ceased. After all the oxide had been added, the solution was diluted with water, neutralised with sodium carbonate, and filtered, and the filtrate was thoroughly extracted with chloroform. The residue which remained after removal of the chloroform consisted of a mixture of sobrerol and the hydroxyketone, but the yield was poor, much of the pinene having been resinified.

Preparation of 8-*Hydroxycarvotanacetone from Pinene.*—A mixture of pinene, mercuric acetate, and water in the proportions given above was shaken for three or four days until the pinene had disappeared, and was then boiled over a free flame for two days, water being added from time to time to replace what had evaporated. During the process, mercurous acetate, and ultimately mercury, together with some resinous matter, separated from the solution. The liquid was then concentrated, neutralised with sodium carbonate and filtered, and the filtrate was shaken with chloroform so long as anything was dissolved. The chloroform solution was washed with water and dried with anhydrous potassium carbonate, and, after removal of the chloroform, a viscid, dark-coloured liquid was obtained. This was purified by fractional distillation under diminished pressure, and finally a product which boiled constantly at 154—155°/10 mm. was obtained. This compound had the properties of the hydroxyketone,

$$C_{10}H_{15}O{\cdot}OH,$$

described by Balbiano (*loc. cit.*), and its semicarbazone had the appearance and the melting point (175—176°) of the semicarbazone which he prepared.

This hydroxyketone is obtained instead of sobrerol when mercuric oxide is added to a solution of pinene in acetic acid if, during the oxidation process, the solution is heated on the water-bath, but much resinous matter is formed, and consequently the yield is not at all satisfactory.

The evidence which led to the conclusion that the hydroxyketone thus obtained from pinene is 8-hydroxycarvotanacetone is as follows. In the first place the melting point of its semicarbazone is almost the same as that of the semicarbazone prepared by Rupe and Schlochoff (*loc. cit.*) from that compound. Secondly, it can be prepared directly from sobrerol. This was effected by oxidising sobrerol with an aqueous solution of mercuric acetate, containing some acetic acid, in a manner similar to that employed in preparing the hydroxyketone from pinene; the product obtained from sobrerol was found to be identical with that obtained from pinene. Therefore the first stage in the oxidation of pinene by mercuric acetate is the formation of sobrerol, and the sobrerol is converted into the hydroxyketone by the further action of the reagent under suitable conditions. In the third place, sobrerol can be obtained by reduction of the hydroxyketone. A solution of the latter in moist ether was treated with sodium in considerable excess of the calculated quantity. After filtration and removal of the ether, the residual solid was purified by crystallisation from benzene, and was identified as inactive sobrerol by determination of its melting point and preparation of its dibromide.

In another direction further information regarding the constitution of the hydroxyketone was gained by its conversion into carvone. A mixture of the hydroxyketone and anhydrous oxalic acid was heated at 80° for fifteen minutes. After cooling, the mass was extracted with chloroform, and the solution was washed with water and dried with anhydrous magnesium sulphate. After removal of the chloroform an oily liquid remained, and by fractional distillation this was separated into two portions, which boiled at about 225° and 236° respectively. The fraction of lower boiling point was analysed with the following result:

0·5089 gave 1·4804 CO_2 and 0·4382 H_2O. C = 80·07; H = 9·56.
$C_{10}H_{14}O$ requires C = 80·00; H = 9·33 per cent.

It was identified as carvone by its physical properties, and by the preparation of its semicarbazone, which was obtained in colourless prisms very readily soluble in methyl alcohol and melting at 154—155°. The fraction of higher boiling point consisted of carvacrol, as was shown by its boiling point and by the production of a green coloration when ferric chloride was added to its alcoholic solution. We found that if the heating of the hydroxyketone with anhydrous oxalic acid was prolonged, the product consisted almost wholly of carvacrol, into which the carvone was transformed by the action of the oxalic acid. We also found that the hydroxyketone is quickly converted into carvacrol by the action of aqueous hydriodic acid at the ordinary temperature.

The consideration of all these facts leaves no doubt that the hydroxyketone, $C_{10}H_{15}O{\cdot}OH$, is 8-hydroxycarvotanacetone.

We desire to express our thanks to Mr. W. J. S. Eastburn for assistance in part of the work, and to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expenses.

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XXXVII.—*The Relationship between the Constitution and the Absorption Spectra of Pyridine and Various Derivatives.*

By JOHN EDWARD PURVIS.

THE absorption spectra of pyridine, picoline, and piperidine have been already studied by Hartley (Trans., 1885, **47**, 685); Baker and Baly (Trans., 1907, **91**, 1122) have also re-examined the spectra of pyridine and the α- and β-picolines, and they found substantially the same results as Hartley. They also examined other pyridine derivatives, their aim being to investigate the effect of the replacement of a CH group of the benzene ring by the nitrogen atom in the pyridine compounds from a consideration that the nitrogen atom has a different type of saturation from that of a carbon atom. They state that the shifts of the heads of the bands of the picoline isomerides were different, and that, expressed in oscillation frequencies, they were:

α-Picoline	3875
β-Picoline	3800

Baly and Collie (Trans., 1905, **87**, 1332) have also pointed out that the introduction of a single group modifies the absorption spectrum of benzene, different types of absorption being produced according to the nature of the group introduced.

Baly and Ewbank (Trans., 1905, **87**, 1355), in the case of disubstituted derivatives of benzene, have shown that the ortho-, meta-, and para-compounds show considerable differences in their absorption curves.

Purvis and Foster (*Proc. Camb. Phil. Soc.*, 1907, **14**, 381), in a comparative study of the absorption curves of collidine and nonachlorocollidine, showed that the character of the curves was not different from that of pyridine and lutidine, except that there were greater shifts towards the red end of the spectrum; the persistence of the collidine curve was a little less than that of lutidine, and also, of course, less than that of pyridine; and the persistence of the nonachlorocollidine curve was slightly less than that of the collidine. The explanation there given was that the chlorine atoms had replaced the hydrogen atoms of the three methyl groups, and this view agreed with the chemical investigation. Expressed in oscillation frequencies, the heads of the bands were:

Pyridine	3950 (Hartley)
2 : 6-Lutidine	3750 (Baker and Baly)
Collidine	3700 (Purvis and Foster)
Nonachlorocollidine	3580 (,, ,,)

The author (*Proc. Camb. Phil. Soc.*, 1908, **14**, 436) pointed out that the effect of adding hydrochloric acid to collidine was precisely the same as in the case of pyridine and lutidine. The acid produced a marked increase in the persistence of the absorption curve, and a slight shift towards the red end. The persistence was much less than that of either lutidine or pyridine hydrochlorides, and corresponded, *pari passu*, with the decreased persistence of the curves of the bases themselves. A heptachlorolutidine, obtained from nonachlorocollidine, was also examined, and, on comparing its curve with the latter, it was seen that the persistence was greatly increased, whilst the shift towards the red end was not so great, but it was greater than that of either collidine or lutidine. The conclusion was that at least one atom of chlorine had entered the nucleus in the change from one compound to the other. Further, it was proved that the persistence of the curve of 3 : 5-dichloropyridine was slightly less than that of 3 : 4 : 5-trichloropyridine, whilst the shift towards the red end was not so great as in the other chlorine compounds. The heads of the bands in oscillation frequencies were:

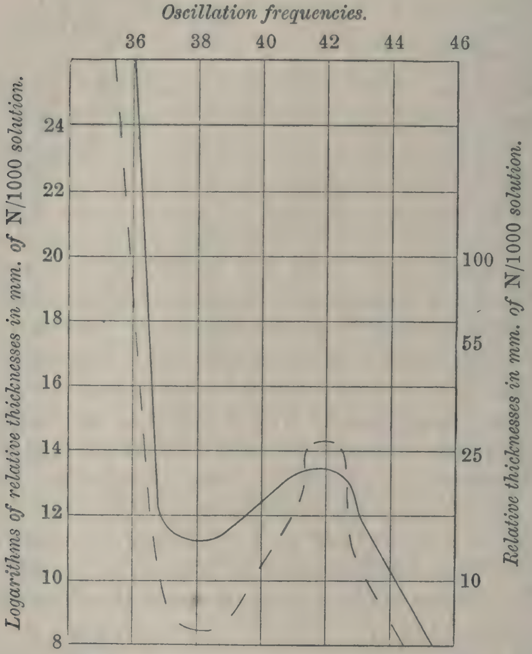
3 : 5-Dichloropyridine	3700 (Purvis)
3 : 4 : 5-Trichloropyridine...............	3650 (Baker and Baly)
2 : 3 : 4 : 5-Tetrachloropyridine	3500 (,, ,,)
Pentachloropyridine................. ..	3400 (,, ,,)

The general form of the absorption curves of 2 : 3 : 5-trichloro- and 3 : 4 : 5-trichloro-pyridines (Purvis, *Proc. Camb. Phil. Soc.*, 1908, **14**, 568) was the same; but that of the 2 : 3 : 5-compound was shifted towards the red end of the spectrum a little further than that of the 3 : 4 : 5-compound, whilst the persistency was very considerably increased. The positions of the bands were:

2 : 3 : 5-Trichloropyridine............	3580
3 : 4 : 5-Trichloropyridine...............	3650

The absorption curves of tetrachloro-2- and -4-aminopyridines were also examined, and compared with the curve of pentachloropyridine. There was a general similarity in the form of the curves, but there was a greater shift towards the red end in the case of tetrachloro-2-aminopyridine compared with that of tetrachloro-4-aminopyridine, and a considerably greater persistency. There was also a greater shift of the curve of the former compound when compared with that of pentachloropyridine, and a less shift in the case of the tetrachloro-4-amino-compound; but the persistency in the case of pentachloropyridine was greater than that of tetrachloro-2-aminopyridine, and very much greater than that of tetrachloro-4-aminopyridine. The positions of the heads of the bands in oscillation frequencies were:

FIG. 1.



Full curve : α-*Picoline.*
Dotted ,, : α-*Picoline hydrochloride.*

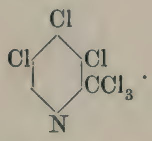
Tetrachloro-2-aminopyridine	3050
Tetrachloro-4-aminopyridine	3550
Pentachloropyridine............................	3400

These results, therefore, indicated that the relative positions and the persistencies of the absorption bands were influenced very considerably by the type and what may be called the spatial positions of the atoms or groups of atoms introduced either into the nucleus or the side-chains. In this direction the aim of this investigation is to give an account of a study of the absorption curves of α-picoline and various derivatives, so as to compare these with the earlier work.

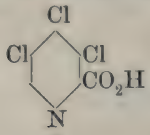
The addition of hydrochloric acid to the solutions of pyridine, 2: 6-lutidine, and collidine has been shown to increase the persistence of the curves very considerably, as well as to shift them towards the red end of the spectrum. In this connexion I have examined the curve obtained when hydrochloric acid was added to a solution of α-picoline, and I found a similar effect.

Fig. 1 gives the curve for α-picoline and that obtained when hydrochloric acid was added to the base. It will be noticed that the addition of the acid has produced a greatly increased persistence, as well as shifted it a little towards the red end. But it should also be pointed out that the persistence of the band of α-picoline is less than that ascribed to 2: 6-lutidine by Baker and Baly; whereas, if the persistence is conditioned by the number or weight of the introduced methyl groups, it should be greater than that of lutidine, just as that of collidine is less than that of lutidine. So that the weighting of the pyridine nucleus by varying numbers of methyl groups does not alone affect the vibrations, and it would seem as if the spatial positions of the substituting groups need to be taken into consideration.

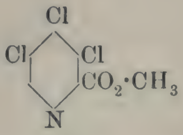
Several chlorine derivatives of α-picoline were also investigated. One of them has been proved by Sell (Trans., 1905, **87**, 799) to have the constitutional formula:



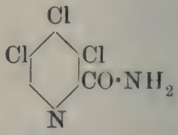
From the absorption curve (Fig. 2), and a comparison of it with the curves in Fig. 1, it will be noticed that the introduction of the chlorine atoms has caused a great shift of the band, and its persistence has been increased. The effect is similar to that observed in the various chlorine compounds of pyridine when the chlorine atoms were introduced into the nucleus, but how far this is modified by the chlorine atoms in the side-chain cannot be judged until a complete series of chlorine compounds of picoline can be obtained and examined. Some indications of this influence are evident from several other compounds of α-picoline which have been investigated. Three derivatives of α-picoline studied in this connexion were trichloropicolinic acid (I), its methyl ester (II), and its amide (III).



(I.)



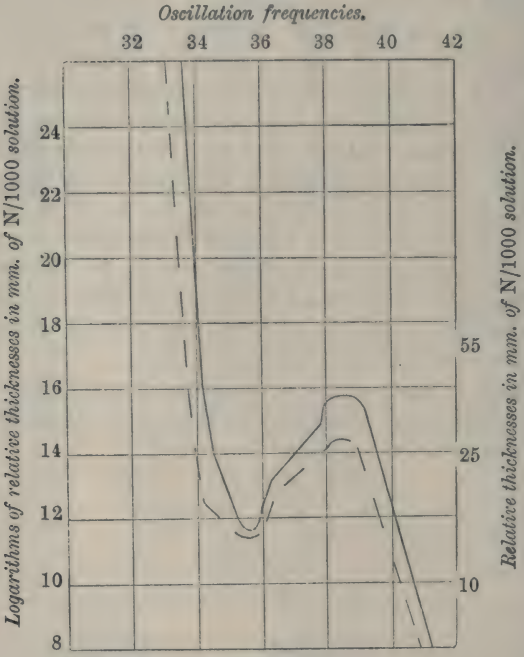
(II.)



(III.)

The absorption curves (Fig. 3) indicate that the bands of the acid and the ester are practically identical, although there is an exceedingly slight shift of the curve of the ester. Moreover, the curves are very like that of hexachloropicoline, although that belonging to the latter compound is not shifted towards the red end quite to the same extent. The curves are practically identical as regards their persistence, although there appears to be less general absorption in the case of the hexachloro-compound. On the other hand, as regards the curve obtained from the amide, although the general form of it is very like that of the other compounds, there

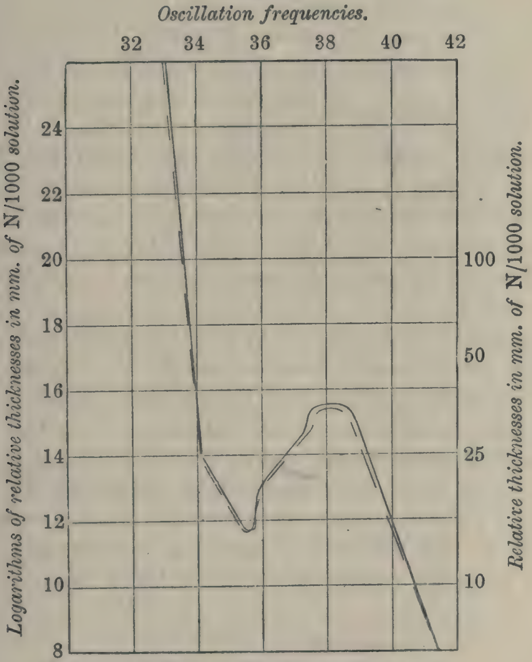
FIG. 2.



Full curve : *Hexachloropicoline.*
Dotted ,, : 2 : 3 : 4-*Trichloropicolinamide.*

is a slight shift, and its persistence is considerably decreased. So that, generally, as in the case of the chlorine derivatives of pyridine and collidine, the chlorine atoms introduced into the nucleus appear to affect the vibrations more powerfully than when they are introduced into the side-chain. It will also be noticed that the effect of the substitution by NH_2 of the OH group of the acid radicle is more marked in this respect than when three chlorine atoms were introduced into the side-chain. Attention may also be drawn to the effect of the introduction of an amino-group by citing the examples of the tetrachloroaminopyridines described before, for such a group appears to modify the absorption bands very considerably either when it is introduced into the nucleus or into a side-chain.

FIG. 3.



Full curve : 2 : 3 : 4-*Trichloropicolinic acid.*
Dotted ,, : *Methyl* 2 : 3 : 4-*Trichloropicolinate.*

The positions of the heads of the bands are:

a-Picoline	3870
a-Picoline hydrochloride	3830
Hexachloropicoline	3570
Trichloropicolinic acid	3560
Trichloropicolinic ester	3550
Trichloropicolinamide	3550

General Conclusions.

The above observations indicate that the vibrations of the pyridine ring and the consequent absorption of light are influenced by various conditions.

(1) The general effect of introducing atoms or groups of atoms into the nucleus is to increase the persistence of the absorption curve as well as to shift it towards the red end of the spectrum, whilst when they are introduced into the side-chains they generally decrease the persistence.

(2) The weighting of the nucleus, however, does not always mean that the absorption curve is shifted towards the red end. The type and the spatial position of the introduced atoms or groups are factors in determining the absorption.

(3) As regards isomeric substances, the spatial positions of the substituting atoms in the nucleus are of considerable importance in influencing the position and the persistence of the absorbed rays.

(4) The substitution of atoms in the side-chains does not exert the same marked influence as when they are substituted in the nucleus.

(5) The addition of hydrochloric acid to collidine and *α*-picoline (as well as to pyridine and lutidine) exerts a marked influence on the vibrations of the nucleus, and the effect is very similar to that produced when chlorine atoms are introduced into the nucleus.

The vibrations of the atoms of a molecule which produce selective absorption have their own distinctive vibrations dependent on their number, weight, nature, type, and orientation. It is further suggested that the vibrations may be considerably influenced by the rays of great refrangibility when light passes through the solutions. On this view, the selective absorption is conditioned by two forces, namely, the inherent vibrations of the atoms, and the vibrations produced by ultra-violet light. Both influences may be in the same direction or in various directions dependent, among other conditions, on the relationship of the atoms; but, in any case, it is conceivable that ultra-violet light may profoundly modify the inherent vibrations of the atoms of the molecule. That the atoms of a nitrogen ring compound may be vibrating in some distinctive form of vibration or pulsation (Baly, Edwards, and Stewart, Trans., 1906, **89**, 514), and different from that produced by the benzene ring, is clear from differences in their absorption bands; but how much is caused by the changing valency of the nitrogen atom and how much by that of other atoms cannot very well be differentiated. In this connexion it cannot be said that the nitrogen atom alone has a variable valency, for it is equally valid to suggest that the other atoms change their valency according to variable conditions. As regards the increased persistence of the absorption curves, the addition of hydrochloric acid to pyridine, α-picoline, lutidine or collidine produces similar effects to that obtained when chlorine is introduced into the nucleus, and it is difficult to realise that the valency of the nitrogen atom is the only conditioning influence. Nevertheless, the fact that fully saturated compounds show no selective absorption in the visible or ultra-violet regions of the spectrum, as in piperidine (Hartley, Trans., 1885, **47**, 685) and *cyclo*hexane (Hartley and Dobbie, Trans., 1900, **77**, 846), emphasises the view that the influence of the saturation of the valencies of the various atoms may be of paramount importance, besides indicating that all the atoms are concerned in the change. Whether such compounds have any bands in the ultra-red has not yet been fully investigated, but the possibility of their presence in this region cannot be ignored, for as regards piperidine, Coblentz (*Astrophys. J.*, 1904, **20**, 207) states that he has observed one band in the ultra-red.

That the vibrations or pulsations of the ring are greatly influenced by the introduction of other atoms or groups of atoms is clear, and the differentiation of tautomeric and isomeric substances by means of changes in their absorption spectra is substantiated. The effect of the introduction of an amino-group, as in the two tetrachloroaminopyridines, is particularly noticeable (Purvis, *loc. cit.*). The nitrogen atom of this group may retain its variable valency like that in the ring, and the effect on the vibrations and the selective absorption would be considerable, although the conditioning influence of the spatial position of the group as a whole appears to be very marked, otherwise the two substances might give similar absorption curves.

If the atoms are connected by Faraday tubes of force, according to the interesting suggestion of Baly and Desch (*Astrophys. J.*, 1906, **23**, 110), and if they are systems of electrons, there should be some possibility of obtaining the Zeeman effect. There would be great difficulty in this, for the absorption bands, as a rule, are broad and diffuse; but if the bands consist of very fine lines, and sufficient dispersion is available to separate the bands into lines, the effect of a strong magnetic field could be observed, and more information would be obtained thereby as to the relation between the atoms and groups of atoms in ring compounds.

Finally, I have to thank Dr. Sell for kindly giving me pure specimens of the substances used in these investigations.

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XXXVIII.—*Benzyl and Ethyl Derivatives of Silicon Tetrachloride.*

By GEOFFREY MARTIN and FREDERIC STANLEY KIPPING.

ALL the four benzyl derivatives of silicon tetrachloride, represented respectively by the following formulæ:

$SiCl_3 \cdot CH_2Ph$, $SiCl_2(CH_2Ph)_2$, $SiCl(CH_2Ph)_3$, $Si(CH_2Ph)_4$,

are known. Tetrabenzylsilicane was prepared long ago by Polis (*Ber.*, 1885, **18**, 1443; 1886, **19**, 1023) by the action of sodium on a mixture of silicon tetrachloride and benzyl chloride, but the other three compounds have only been obtained quite recently with the aid of the Grignard reagent (compare Robison and Kipping, Trans., 1908, **93**, 439). Of all the alkyl and aryl compounds of silicon which have been prepared in these laboratories during the last few years, these benzyl derivatives are, perhaps, the most accessible; by the process described later, a modified method of applying the Grignard reagent, the mono-, di-, and tri-derivatives are easily produced and isolated.* When decomposed with water these chlorides give three different types of silicon compounds, namely, an acid, a silicone (or its hydrol), and a silicol respectively: $C_6H_5 \cdot CH_2 \cdot SiO_2H$, $(C_6H_5 \cdot CH_2)_2Si(OH)_2$, $(C_6H_5 \cdot CH_2)_3Si \cdot OH$. These compounds, being well adapted for the purpose, have been investigated with the object of studying the chemical behaviour and characteristic reactions of the respective types of silicon compounds, and of comparing their properties with those of the corresponding types of carbon compounds.

The first matter to which we directed our attention was a study of the conditions under which tribenzylsilicol might be converted into the corresponding oxide. In the course of recent work, it has been found that many of the silicols, such as benzylethylpropylsilicol, are readily changed into oxides, and that these oxides are generally formed together with the silicol when a chloride of the type R_3SiCl is decomposed with cold water, or with a solution of sodium carbonate (Kipping, Trans., 1907, **91**, 209, 717). The spontaneous conversion of some silicols into the oxides at the ordinary temperature has also been observed (Kipping, Trans., 1907, **91**, 726; Robison and Kipping, Trans., 1908, **93**, 450). In other cases, as, for example, in that of triphenylsilicyl chloride, the silicol alone seems to be formed when the chloride is treated with water, although the silicol may be transformed into the oxide by heating it with an alcoholic solution of hydrogen chloride (Kipping and Lloyd, Trans., 1901, **79**, 449). Tribenzylsilicyl chloride behaves like triphenylsilicyl chloride; although the only product of its decomposition by water is the corresponding silicol (Robison and Kipping, *loc. cit.*), the latter is converted into tribenzylsilicyl oxide, $[Si(CH_2{\cdot}C_6H_5)_3]_2O$, when it is heated with concentrated hydrochloric acid. That the formation of the oxide under these conditions is not merely a temperature effect is shown by the fact that when the silicol is heated alone at 150° the oxide is not produced; even at higher temperatures, although the silicol suffers some decomposition on prolonged heating, it does not yield oxide in quantities which can be detected. Boiling acetic anhydride, which might be expected to transform the silicol into the oxide much more readily than does hydrochloric acid, has no action; acetyl chloride also does not bring about the formation of oxide, but converts the silicol quantitatively into tribenzylsilicyl chloride:

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* Tetrabenzylsilicane is also formed by this method, but so far it has only been obtained as a by-product, and the best method of preparing it has not been investigated.

$$Si(C_7H_7)_3{\cdot}OH + CH_3{\cdot}CO{\cdot}Cl = Si(C_7H_7)_3Cl + CH_3{\cdot}CO_2H.$$

In a similar manner the silicol is transformed into the chloride when it is heated with excess of benzoyl chloride. Acid chlorides rarely act in this way on ordinary alcohols, although cases are not unknown in which fatty compounds, such as dimethylethylcarbinol, are converted into their chlorides by acetyl chloride. The above reactions therefore indicate a considerable difference between an alcohol and a silicol, and seem to afford fresh evidence of the fact that a silicol possesses a more "basic" character than an alcohol, as, indeed, is only to be expected, since silicon, from its position in the periodic system, is known to be more electropositive than carbon. Considering the rapidity with which the chlorine atom is displaced by hydroxyl when silicon tetrachloride, or any of its mono-, di-, or tri-alkyl derivatives, is treated with water, it is not a little surprising that tribenzylsilicyl chloride should be formed in the above manner. The substitution of chlorine for an ethoxy-group united with silicon was observed by Ladenburg (*Annalen*, 1872, **164**, 309), who found that at 200°, diethoxydiethylsilicane, $SiEt_2(OEt)_2$, was transformed into ethoxydiethylsilicyl chloride by the action of acetyl chloride, whereas at 250° it was converted into diethylsilicon dichloride, $SiEt_2Cl_2$, by the action of benzoyl chloride. These changes are obviously comparable to those which we have observed, although perhaps they do not afford such striking examples of the difference between compounds of carbon and those of silicon. The readiness with which tribenzylsilicol is converted into the chloride by the action of acetyl chloride seemed to indicate that the transformation of the silicol into the oxide with the aid of hydrochloric acid might be due to the initial formation of chloride, which reacted with the silicol:

$$Si(CH_2\cdot C_6H_5)_3Cl + Si(CH_2\cdot C_6H_5)_3\cdot OH = [Si(CH_2\cdot C_6H_5)_3]_2O + HCl.$$

Some confirmation of this view, which would also account for the formation of oxide on treating the chloride with water, is afforded by the fact that tribenzylsilicyl oxide is readily formed when a mixture of the chloride and the silicol in xylene solution is heated with sodium; on the other hand, it was found that the conversion of the silicol into the oxide may also be brought about by heating the former with a 20 per cent. solution of sodium hydroxide. The re-conversion of the oxide into the silicol has not yet been accomplished; hot highly concentrated potassium hydroxide solution slowly decomposes the oxide into toluene and potassium silicate.

The acids of the type $R\cdot SiO_2H$, where R represents an alkyl group, differ very greatly from the corresponding carboxylic acids in physical and in chemical properties. Silicopropionic acid or ethylmetasilicic acid, $C_2H_5\cdot SiO_2H$, for example, is an amorphous substance insoluble in all common solvents except potassium hydroxide solution. Silicophenylacetic acid (benzylmetasilicic acid), $C_6H_5\cdot CH_2\cdot SiO_2H$, prepared by decomposing benzylsilicon trichloride with water, differs from ethylmetasilicic acid in being readily soluble in ether and many other organic solvents, and in being a resinous substance of low melting point. Thinking that the presence of a relatively large aryl radicle might so modify the properties of the $\cdot SiO_2H$ group as to render silicophenylacetic acid comparable with a carboxylic acid, we made some experiments with this silicon compound in the hope of preparing some of its derivatives; but we soon found that it showed little resemblance to phenylacetic acid, its carbon analogue; it is insoluble in sodium carbonate solution and in ammonium hydroxide, does not form stable salts with organic bases, such as aniline or phenylhydrazine, and cannot be esterified by the usual method. According to Ladenburg (*Annalen*, 1874, **173**, 151, 166), phenylmetasilicic acid, $C_6H_5\cdot SiO_2H$, and tolylmetasilicic acid, $CH_3\cdot C_6H_4\cdot SiO_2H$, are converted into their anhydrides when they are heated at 100°. Benzylmetasilicic acid, however, seems to undergo no change at this temperature, nor does it seem to give an anhydride when it is heated at 150° during seven hours, or boiled with acetic anhydride during forty-eight hours.

The ethyl ester of benzylorthosilicic acid, $C_6H_5\cdot CH_2\cdot Si(OEt)_3$, may be obtained by treating the trichloride with alcohol; it is a colourless liquid boiling at 250—256°/763 mm. It is completely decomposed by a hot concentrated solution of potassium hydroxide, giving toluene, ethyl alcohol, and a silicate. The decomposition of benzyl derivatives of silicon by concentrated potassium hydroxide solution seems to be a general reaction; just as sulphobenzylethylpropylsilicyl oxide gives toluenesulphonic acid (Kipping, Trans., 1908, **93**, 472), so the ester just mentioned, the corresponding acid, and tribenzylsilicol are all readily decomposed with formation of toluene.

Although tetra-alkyl and tetra-aryl derivatives of silicane may be prepared from silicon tetrachloride by the Fittig reaction (compare Polis, *loc. cit.*; Kipping and Lloyd, Trans., 1901, **79**, 449), our experiments seem to show that it is very difficult, if not impossible, to bring about the union of two silicon atoms by heating compounds of the type SiR_3Cl or $SiRCl_3$ with sodium or potassium. Many attempts have been made to prepare the compound $(C_6H_5{\cdot}CH_2)_3Si{\cdot}Si(CH_2{\cdot}C_6H_5)_3$ from tribenzylsilicyl chloride, but so far without success; even potassium at high temperatures fails to give the desired result.

The four ethyl derivatives of silicon tetrachloride, namely: $SiCl_3{\cdot}C_2H_5$, $SiCl_2(C_2H_5)_2$, $SiCl(C_2H_5)_3$, and $Si(C_2H_5)_4$, were obtained long ago by Friedel, Crafts, and Ladenburg. Although these compounds are formed by the interaction of magnesium ethyl bromide and silicon tetrachloride, and although silicon ethyl trichloride may be prepared in this way without any great difficulty (Kipping, Trans., 1907, **91**, 209), the isolation of diethylsilicon dichloride and triethylsilicyl chloride from the products of this reaction is a very troublesome process, owing doubtless to the small differences in the boiling points of the three chloro-derivatives. Many experiments have been made in order to ascertain the most suitable conditions for the preparation of these ethyl derivatives, but in all cases, employing quantities corresponding with 2—2½ molecules of magnesium ethyl bromide for every molecule of silicon tetrachloride, the product is a complex mixture which seems to contain, not only all the four ethyl derivatives mentioned above, but also more complex substances of high boiling points. The bulky mass of magnesium salt which remains after separating the various ethyl compounds referred to above is not completely soluble in water, but contains a very considerable proportion of some silicon compound or compounds, which, when treated with water, affords an insoluble, yellow, amorphous product. The constitution of this (impure) substance seems to be analogous to that of silico-oxalic acid (Friedel and Ladenburg, *Annalen*, 1880, **203**, 250) and silico-mesoxalic acid (Gattermann and Ellery, *Ber.*, 1899, **32**, 1114), inasmuch as it is slowly decomposed by water, much more rapidly by cold aqueous alkali, with evolution of hydrogen;

although many attempts have been made to isolate a pure compound from this product, so far they have been unsuccessful, owing to the insolubility of the material in all media except aqueous alkalis. Analysis of the crude preparation seems to indicate that it consists principally of a silicon compound having the composition $C_2H_8O_4Si_2$. We hope to obtain further information on this point by examining the products, apparently of a similar character, which are obtained when silicon tetrachloride is treated with an aryl bromide in the presence of magnesium.

Our chief object in preparing diethylsilicon dichloride, $Si(C_2H_5)_2Cl_2$, was to ascertain whether this compound would yield, on decomposition with water, a hydrol, $Si(C_2H_5)_2(OH)_2$, corresponding with that (or those) obtained from dibenzylsilicon dichloride, $Si(C_7H_7)_2Cl_2$ (Robison and Kipping, *loc. cit.*). It seems, however, that dihydroxydiethylsilicane does not exist, and that the dichloride is directly converted into the silicone, $SiEt_2O$, which then polymerises, giving a compound of high molecular weight.

EXPERIMENTAL.

Preparation of Benzyl Derivatives of Silicon Tetrachloride. A Modified Method of Applying the Grignard Reagent.

In preparing benzylethylsilicon dichloride (Kipping, Trans., 1907, **91**, 717), it is impossible to know exactly the most suitable proportions of magnesium and of benzyl chloride to employ, owing to the formation of variable amounts of dibenzyl. The presence of suspended magnesium chloride in the ethereal solution of the Grignard reagent is also troublesome, and the separation of the dibenzyl from the benzylethylsilicon dichloride necessitates repeated fractional distillation. It occurred to one of us that all these disadvantages might be overcome, and that the actual preparation of the Grignard reagent might be obviated by gradually dropping benzyl chloride (1 molecule) into an ethereal solution of ethylsilicon trichloride (1 molecule) to which magnesium powder (1 atom) had been added. This modification of the usual method proved very successful; the addition of the benzyl chloride can be exactly regulated, the formation of dibenzyl is avoided, the preparation and isolation of the product takes much less time, and the yield seems to be greater than by the original process (compare Luff and Kipping, Trans., 1908, **93**, 2004). In preparing the benzyl derivatives of silicon tetrachloride, this modified method of applying the Grignard reagent has been utilised. The theoretical quantity of magnesium, placed in a flask, is covered with an ethereal solution of silicon tetrachloride, and a small quantity of benzyl chloride is run in. The reaction is started by adding a little magnesium benzyl chloride prepared in a test-tube, and as soon as it becomes fairly vigorous, the contents of the flask are cooled in ice. The rest of the benzyl chloride is then slowly run in, stirring all the time, and afterwards the contents of the flask are heated, if necessary, using a reflux condenser. The product is separated from the magnesium salt in the usual manner (Kipping, Trans., 1907, **91**, 216), and purified by fractional distillation.

Even when quantities of magnesium corresponding with 1, 2, or 3 atoms, and of benzyl chloride corresponding with 1, 2, or 3 molecules, are used, the desired product always contains a considerable proportion of the other two benzylsilicon chlorides. The great difference between the boiling points of the mono-, di-, and tribenzyl derivatives, however, renders their separation an easy matter, and details may be omitted. Hitherto no experiments have been made using 4 atoms of magnesium to 1 molecule of silicon tetrachloride, but small amounts of tetrabenzylsilicane have been isolated in preparing the di- and tri-benzyl derivatives.

Benzylsilicon trichloride, $C_6H_5\cdot CH_2\cdot SiCl_3$, is obtained from the crude fraction of the product distilling over between about 135 and 150°/100 mm. It is a colourless liquid, boiling at 140—142°/100 mm., and has been recently described by Melzer (*Ber.*, 1908, **41**, 3390), who gives its boiling point as 94—96°/11 mm.

Dibenzylsilicon dichloride, $(C_6H_5\cdot CH_2)_2SiCl_2$, is prepared by fractionally distilling the crude product collected at 240—250°/100 mm. It melts at 50—52°, and boils at 241—245° (Robison and Kipping, *loc. cit.*).

Tribenzylsilicyl chloride melts at 141°, and boils at about 300—360°/100 mm. The substance is only slowly decomposed when thrown into water, several hours elapsing before it is completely transformed into tribenzylsilicol.

Experiments on the Conversion of Tribenzylsilicol into Tribenzylsilicyl Oxide, $[Si(CH_2\cdot C_6H_5)_3]_2O$.

The decomposition of tribenzylsilicyl chloride with water leads to the production of tribenzylsilicol (m. p. 104°), apparently quite free from oxide. When, however, the silicol is heated with concentrated aqueous hydrochloric acid (the presence of alcohol does not hasten the process, but if anything retards it), it melts to an oil, which gradually changes in the course of many hours into the solid oxide. The oxide was crystallised from a mixture of chloroform and light petroleum, the unchanged silicol remaining in the mother-liquors:

0·1443 gave 0·4259 CO_2 and 0·0878 H_2O. C = 80·5; H = 6·8.
0·3837 „ 0·0748 SiO_2. Si = 9·1.
$C_{42}H_{42}OSi_2$ requires C = 81·4; H = 6·8; Si = 9·1 per cent.

Tribenzylsilicyl oxide crystallises in compact, rhomboidal plates, melting at 205°. It is very soluble in chloroform, and sparingly so in light petroleum or alcohol. It is very stable, a boiling concentrated solution of potassium hydroxide having little action on it. Attempts to convert the oxide into the silicol or into tribenzylsilicyl chloride with the aid of phosphorus pentachloride were unsuccessful.

Although tribenzylsilicol passes into the oxide when it is heated with hydrochloric acid, this transformation does not occur when the silicol is heated alone; at 150° it undergoes very little change, whereas when it is heated at 170° during two or three days it is almost entirely decomposed, giving a viscid, yellow fluid. The silicol is also unchanged when it is boiled with acetic anhydride during several hours.

Action of Acetyl and Benzoyl Chlorides on the Silicol.

When tribenzylsilicol is warmed with a large excess of acetyl chloride during some hours and the solution then evaporated, colourless crystals are deposited. This compound was proved to be identical with tribenzylsilicyl chloride (m. p. 141°), and the reaction seemed to have taken place quantitatively, inasmuch as neither silicol nor oxide could be detected in the crude product.

As it seemed rather surprising that this silicol should give the chloride, whereas triphenylsilicol, according to Kipping and Lloyd (*loc. cit.*), gives an acetyl derivative when it is boiled with acetyl chloride, the behaviour of triphenylsilicol was examined.

The pure compound was heated with excess of acetyl chloride during three hours, the solution evaporated, and the residue crystallised from light petroleum. This product melted at 88—89°, and was identified as triphenylsilicyl chloride. It must be concluded, therefore, that the "triphenylsilicyl acetate" (m. p. 91·5°) described by Kipping and Lloyd (*loc. cit.*) was, in fact, triphenylsilicyl chloride.*

Tribenzylsilicol also yields the corresponding chloride when it is boiled with excess of benzoyl chloride during several hours, and in this case also the reaction seems to take place quantitatively;

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* The analyses of this "acetate" and, in fact, all the analyses given in this paper by Kipping and Lloyd, except that of triphenylsilicol, were carried out by Lloyd.—F. S. K.

attempts to prepare the benzoyl derivative of the silicol by the Schotten-Baumann method were unsuccessful.

When powdered tribenzylsilicol is thrown into a hot, very concentrated solution of potassium hydroxide, it is decomposed with effervescence, toluene being evolved so rapidly that the hydrocarbon may be ignited at the mouth of the tube. Prolonged boiling with the dilute agent (20 per cent.) also decomposes the silicol slowly, but at the same time a considerable quantity of tribenzylsilicyl oxide is formed. When alcoholic potash is used, the results are similar, but the yield of oxide seems to be diminished.

Silicophenylacetic acid (benzylmetasilicic acid), $C_6H_5{\cdot}CH_2{\cdot}SiO_2H$. —When prepared by pouring benzylsilicon trichloride into water, this acid is obtained as a viscid, white, sticky mass, which, on standing, solidifies. When its ethereal solution is evaporated, it remains as a yellow, glue-like mass, which, after prolonged heating at 95° to expel ether, turns into a hard solid when allowed to cool. Both preparations gradually soften when heated, and at 70° are quite liquid. No definite melting point was observed, although Melzer, who recently prepared this compound, gives it the melting point 65—66° (*loc. cit.*). For analysis the samples were heated at 100° until constant, and, as the acid retains ether with great pertinacity, prolonged heating was necessary:

0·1254 gave 0·2548 CO_2 and 0·0652 H_2O. C = 55·4; H = 5·7.
0·2226 „ 0·904 SiO_2. Si = 19·09.
$C_7H_8O_2Si$ requires C = 55·1; H = 5·3; Si = 18·62 per cent.

In a fused condition the acid is extraordinarily coherent, and can be drawn out into fine threads of great length. The substance is an excellent glue, and adheres to glass, paper, wood, and porcelain very firmly. It has the advantage of not being acted on by cold water, but hot water softens it. Methyl and ethyl alcohols dissolve it somewhat sparingly; ether, ethyl acetate, acetone, aniline, and phenylhydrazine dissolve it readily.

Silicophenylacetic acid dissolves rapidly in a warm, very concentrated solution of potassium hydroxide, giving toluene and potassium silicate. In a cold dilute (3—4 per cent.) solution of potassium hydroxide, it dissolves only very slowly, and is reprecipitated, apparently unchanged, on acidifying. Sodium carbonate solution appears to have no action on the acid.

The acid mixes in all proportions with aniline and with phenylhydrazine, but the salts, if formed, are completely decomposed by water, as the whole of the bases may be removed by distillation in steam, the acid being recovered unchanged.

A sample of silicophenylacetic acid was heated at 150—160°

during eight hours; another specimen was boiled with acetic anhydride during forty-eight hours. In both cases, as far as could be ascertained, the acid was unchanged; it melted completely below 70°, and was readily soluble in ether.

Ethyl Benzylorthosilicate, $C_6H_5{\cdot}CH_2{\cdot}Si(O{\cdot}C_2H_5)_3$.—Attempts to prepare an ester by boiling silicophenylacetic acid with ethyl alcohol in the presence of hydrochloric acid were unsuccessful. On adding benzylsilicon trichloride to anhydrous ethyl alcohol, the solution becomes hot, and a rapid evolution of hydrogen chloride takes place. On fractionally distilling the product under diminished pressure, two compounds may be isolated, namely, the normal ester, $C_6H_5{\cdot}CH_2{\cdot}Si(O{\cdot}C_2H_5)_3$, and the oxide, $[C_6H_5{\cdot}CH_2{\cdot}Si(O{\cdot}C_2H_5)_2]_2O$.

Melzer (*loc. cit.*), using the same method, has isolated the former of these substances.

Ethyl benzylorthosilicate is a colourless, mobile oil, possessing a faint, not unpleasant, odour, and boiling at 170—175°/70 mm., 250—256°/763 mm.:

0·1687 gave 0·3782 CO_2 and 0·1325 H_2O. C = 61·13; H = 8·71.
0·2464 ,, 0·0584 SiO_2. Si = 11·15.
$C_{13}H_{22}O_3Si$ requires C = 61·27; H = 8·72; Si = 11·16 per cent.

Neither cold nor hot water dissolves the oil in noticeable quantity, but if it is left in contact with cold water during some days, hydrolysis seems to occur.

The ester is only very slowly hydrolysed by dilute aqueous potassium hydroxide solution at the ordinary temperature, but a hot, concentrated solution of potassium hydroxide decomposes it with effervescence, toluene being liberated. The ester is also immediately decomposed by dilute sulphuric acid, apparently with formation of silicophenylacetic acid.

Benzyldiethoxysilicyl oxide, $[C_6H_5{\cdot}CH_2{\cdot}Si(O{\cdot}C_2H_5)_2]_2O$, is a yellow oil, having a faint odour, and boiling at 256—260°/75 mm. It is insoluble in water, but miscible with ether:

0·1531 gave 0·3405 CO_2 and 0·1100 H_2O. C = 60·65; H = 8·05.
0·1370 ,, 0·0380 SiO_2 Si = 13·04.
$C_{22}H_{34}O_5Si_2$ requires C = 60·67; H = 7·88; Si = 13·05 per cent.

Action of Sodium on Tribenzylsilicyl Chloride.

Several attempts have been made to remove the chlorine from tribenzylsilicyl chloride, and thus to cause the silicon atoms to unite, but the desired result has not been attained. In one of the first experiments, a sample of the chloride, which had been kept for some time, was dissolved in xylene, and the solution heated at its boiling point with excess of sodium; on cooling, the solution deposited a large quantity of pure tribenzylsilicyl oxide.

As this result seemed to be due to the presence of tribenzyl silicol in the sample of chloride used, and as an analysis of the latter showed that it contained chlorine corresponding with only 92 per cent. of tribenzylsilicyl chloride, the experiment was repeated with a sample of the pure chloride obtained by heating the impure preparation with excess of acetyl chloride. In this case no appreciable action occurred at the boiling point of xylene, so the xylene was distilled off, and the mixture of sodium and tribenzylsilicyl chloride heated at 200—220° during three and a-half hours. After cooling, the product was treated with methyl alcohol to dissolve the unchanged sodium, and the residue was dissolved in chloroform; on evaporating, crystals of tribenzylsilicyl oxide (m. p. 204·5°) were obtained. The methyl-alcoholic solution contained a small quantity of tribenzylsilicol. Several other experiments were tried, using potassium instead of sodium and varying the conditions, but the oxide was always obtained. Even when heated with potassium at 230° during several hours, the chloride seemed to give no appreciable quantity of potassium chloride, and there was no indication of the formation of the desired product.

Similar experiments were made using benzylsilicon trichloride and benzylethylpropylsilicyl chloride instead of the tribenzyl derivative, but the results were equally unsatisfactory.

Preparation of Diethylsilicon Dichloride.

First Method.—When silicon tetrachloride, largely diluted with ether, is gradually treated in the cold with an ethereal solution of magnesium ethyl bromide (2½ molecules) in the manner described in the preparation of ethylsilicon trichloride (Kipping, Trans., 1907, **91**, 214), and the mixture then heated in a reflux apparatus during three to four hours, a large quantity of magnesium salt is precipitated. The ethereal solution of the product, together with the ethereal washings from the magnesium salt, give, on evaporation, a further deposit of solid matter, which is separated by filtration through asbestos. The fuming liquid which is thus obtained is a complex mixture. When fractionally distilled under atmospheric pressure, the thermometer rises slowly and regularly from about 95° to 150°, and at this temperature a considerable proportion (about 25 per cent.) of the total product remains as a dark-coloured, but mobile, residue. On redistilling the crude distillate, using a rod-and-disk column, or even a Young's three-chamber column, it is no easy matter to isolate the components of this mixture; but after many operations, ethylsilicon trichloride (b. p. 100°), diethylsilicon dichloride (b. p. 128—130°), and triethylsilicyl chloride (b. p. 143°) may be obtained in a pure state. The yield of the dichloride is only about 18 grams from 160 grams of silicon tetrachloride.

Various samples of the dichloride were analysed by decomposing with ammonia and titrating with silver nitrate. The results ranged from 44·1 to 44·8 per cent. of chlorine, whereas $Si(C_2H_5)_2Cl_2$ requires $Cl=45·2$ per cent.

Second Method.—When silicon tetrachloride (1 molecule), magnesium (2 molecules), and some ether are placed together in a flask, and ethyl bromide is added in small quantities, some time elapses before any change sets in, and it may be necessary to warm gently; but when the reaction has once started, it proceeds vigorously, with a considerable development of heat. The flask is therefore cooled in ice, and the rest of the ethyl bromide (2 molecules) added gradually from a tap funnel, the contents of the flask being rapidly stirred. During this process the magnesium gradually changes to magnesium salt, but the latter is very different from the bulky, somewhat gelatinous or colloidal compound which is formed when silicon tetrachloride is treated with an ethereal solution of magnesium ethyl bromide, and takes the form of a heavy, coarsely crystalline powder. As soon as the whole of the ethyl bromide has been added, the ethereal solution of the silicon compound may be separated by filtering and extracting in the usual way (Kipping, Trans., 1907, **91**, 216), or by gradually heating the flask to 200° in an oil-bath until distillation ceases. The crude mixture of silicon compounds, obtained after evaporating the ether, behaves very much like that produced by the first method, and when distilled with a rod-and-disk column the thermometer rises slowly and regularly from about 95° to 150°, at which temperature a considerable proportion of a dark-coloured, mobile oil still remains in the distilling flask. By repeated fractional distillation, ethylsilicon trichloride and diethylsilicon dichloride may be obtained in a state of purity, but the yield of both is very poor, and a large proportion of the silicon in the original silicon tetrachloride seems to remain in the form of some complex compound in the magnesium chlorobromide (see below).

Third Method.—When a mixture of silicon tetrachloride (1 mol.) and ethyl bromide (2 mols.), diluted with ether, is placed in a flask, and, after starting the reaction with the aid of a little magnesium ethyl bromide, magnesium powder is added in small quantities at a time to the well-cooled and vigorously-stirred solution, a change occurs similar to that observed in the second method of preparation.

The crude product, isolated in a similar manner, also seems to have much the same composition as that obtained by the second method, but the yield was no better.

Diethylsilicone, $(C_2H_5)_2SiO$.

When pure diethylsilicon dichloride is poured into cold water, it is immediately decomposed, giving an oil of about the same consistency as glycerol; this oil seems to be the silicone, and not the corresponding hydrol, $(C_2H_5)_2Si(OH)_2$, because when it is merely washed with water until free from hydrochloric acid, and is then kept over sulphuric acid, warming gently from time to time until constant in weight, the liquid so obtained has the composition $Si(C_2H_5)_2O$, as shown by the following analyses:

0·1703 gave 0·2908 CO_2 and 0·1464 H_2O. C = 46·6; H = 9·5.
0·1146 „ 0·0676 SiO_2. Si = 27·5.
$C_4H_{10}OSi$ requires C = 46·8; H = 9·8; Si = 27·7 per cent.

Diethylsilicone is insoluble or practically insoluble in water, but is miscible with ether, benzene, acetone, and other organic solvents.

The molecular weight of this silicone was determined in various solvents, with the following results:

By the cryoscopic method:

0·3574 in 21·04 benzene gave $\Delta t = -0·13$. M.W. = 694.

By the ebullioscopic method: (I.) in benzene, (II.) in chloroform:

	Substance.	Solvent.	E.	M.W.
I.	0·936	15·1	0·26	636
II.	0·9212	15·0	0·41	545
	0·7947	17·7	0·31	530

As diethylsilicone requires M.W. = 102, these results show that the silicone is highly polymerised in these solvents; but except in one experiment, no evidence of the existence of definite polymeric forms has been obtained. In the case referred to, the dichloride was poured into a little distilled water, and the water and hydrochloric acid were expelled by heating on the water-bath; the product, when cooled, consisted of a transparent, yellow jelly. Repeated attempts were made to prepare this gelatinous substance again in a similar manner, but the silicone was always obtained in the oily form described above.

By-products formed in the Preparation of Diethylsilicon Dichloride.

Although triethylsilicyl chloride is obtained as a by-product in preparing the diethyl derivative, very little, if any, tetraethylsilicane (b. p. 154°) seems to be formed under the conditions described above; as already stated, a considerable proportion of the crude product does not boil below 150°, but when this residue is fractionally distilled, the thermometer rises regularly up to about 200°, and even after repeated distillation no tetraethylsilicane or other compound can be isolated. That the reactions which occur in the preparation of the dichloride are very complex is also shown by an examination of the solid residue from which the volatile silicon compounds have been separated by extracting with ether or by distillation; this residue, although consisting principally of magnesium salts, contains a moderate proportion of some compound (or compounds) which is insoluble in water or dilute acids, and which remains as a yellow solid on dissolving the magnesium salts. When left in contact with water at the ordinary temperature, this solid very slowly evolves hydrogen, and when warmed with potassium hydroxide solution it dissolves readily, hydrogen being rapidly evolved. As the product is insoluble in all ordinary solvents, various samples were successively extracted with water, hydrochloric acid, alcohol, ether, etc., and the dried residues analysed. The results, as might be expected from the method of purification, were not concordant, but they seemed to show that the main constituent of the yellow solid is a substance of the composition $C_2H_8O_4Si_2$. When the solid is dissolved in aqueous potassium hydroxide, and the solution is then treated with excess of dilute sulphuric acid, a gelatinous acid is precipitated; this acid seems to have the composition $C_2H_6O_4Si_2$, but as it is insoluble in all ordinary solvents, and as fractional precipitation gave products containing different proportions of silicon, we have not been able to establish its nature. As far as any conclusion can be drawn at present, it would seem that the original yellow solid is possibly a compound of the constitution $C_2H_5 \cdot Si(OH)_2 \cdot SiO_2H$, which is decomposed by potassium hydroxide, giving the potassium salts of ethylmetasilicic acid and metasilicic acid, with evolution of hydrogen:

$$C_2H_5 \cdot Si(OH)_2 \cdot SiO_2H + 3KOH = C_2H_5 \cdot SiO_2K + K_2SiO_3 + H_2 + 2H_2O.$$

Further experiments with these and with similar compounds obtained by the interaction of silicon tetrachloride, magnesium, and aryl halides are in progress.

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XXXIX.—*Esterification Constants of Substituted Acrylic Acids. Part III.*

By JOHN JOSEPH SUDBOROUGH and JAMES MYLAM GITTINS.

IN continuation of the work on the esterification constants of unsaturated acids (Trans., 1905, **87**, 1840; 1907, **91**, 1033; see also Trans., 1898, **73**, 81), we have obtained the values given in the table on p. 319.

The experiments were all made at 15° with hydrogen chloride as catalyst and with a specimen of Kahlbaum's No. 1 methyl alcohol which had been distilled over calcium. This alcohol gave a constant for cinnamic acid which varied by only 1 to 2 per cent. from the value previously obtained, so that the numbers recorded in this paper are directly comparable with those determined by Sudborough and Roberts (Trans., 1905, **87**, 1840). The alcohol used was not completely dehydrated, since on further treatment with calcium a product was obtained which gave a somewhat higher (15—20 per cent.) constant for cinnamic acid (compare Gyr, *Ber.*, 1908, **41**, 4322). We decided, however, to use the alcohol which had been treated once with calcium, in order that the constants obtained should be directly comparable with those determined previously.

1. The results obtained confirm the generalisation previously drawn, namely, that an αβ-unsaturated acid (a substituted acrylic acid) is esterified much less readily than its saturated analogue. The following table gives a comparison of the values, $E^{15°}_{MeOH}$, so far

αβ-Unsaturated acid.	$E^{15°}_{MeOH}$.	Saturated acid.	E_{MeOH}.
Crotonic	1·28 [1]	*n*-Butyric	50·0 [3]
Cinnamic	0·937 [1]	β-Phenylpropionic	47·3
Methyl hydrogen fumarate	1·79 [1]	Methyl hydrogen succinate	17·25 [2]
,, ,, maleate	0·86 [1]		
β-Ethylacrylic	1·5 [4]	*n*-Valeric	53·5 [3]
β-Furfurylacrylic	0·718 [1]	β-Furfurylpropionic	43·9
β-Furfuryl*allo*acrylic	0·379 [1]		
Phenylpropylideneacetic	1·32	δ-Phenyl-*n*-valeric	39·5
Atropic	0·187 [1]	Hydratropic	9·6
Tiglic	0·411 [5]	Methylethylacetic	12·6 [5]
Angelic	0·116 [5]		
β-Dimethylacrylic	0·285 [5]	*iso*Valeric	12·3 [5]
Trimethylacrylic	0·042 [5]	Methyl*iso*propylacetic	1·25 [5]
α-Methylacrylic	0·824 [5]	*iso*Butyric	33·6 [5]
αβ-Oleic	1·36	Palmitic	49·7 [3]
α-Phenylcinnamic	0·126 [1]	Phenylbenzylacetic	3·58
α-Phenyl*allo*cinnamic	0·00288 [1]		

[1] Sudborough and Roberts, Trans., 1905, **87**, 1843.

[2] Bone, Sudborough, and Sprankling, Trans., 1904, **85**, 540.

[3] Sudborough and Gittins, Trans., 1908, **93**, 211.

[4] Sudborough and Thomas, Trans., 1907, **91**, 1033. The numbers previously obtained have been doubled, as the alcohol used gave low numbers.

[5] Unpublished results of Sudborough and M. J. P. Davies.

determined for *αβ*-unsaturated acids and for their saturated analogues.

Since the appearance of our last paper (Trans., 1907, **91**, 1033), Kailan (*Monatsh.*, 1907, **28**, 1137) has confirmed the retarding influence of an *αβ*-ethylene linking in the case of cinnamic acid.

2. The effect of a triple linking in the *αβ*-position is shown in the following series of acids:

Acetylenic acid.	$E_{\text{MeOH}}^{15^\circ}$.	Olefinic acid.	$E_{\text{MeOH}}^{15^\circ}$.	Saturated acid.	$E_{\text{MeOH}}^{15^\circ}$.
Tetrolic............	1·29	Crotonic.........	1·28 [1]	*n*-Butyric...............	50 [2]
Phenylpropiolic.	0·64 [1]	Cinnamic	0·94	*β*-Phenylpropionic...	47·3

The numbers show that a triple linking in the *αβ*-position has much the same effect on the esterification by the catalytic method as a double linking in the same position.

3. The effect of a double linking in a position other than the *αβ* is extremely well indicated in the values we have obtained. In the case of a *βγ*-unsaturated acid, the constant is always higher than that for the saturated analogue, as shown by the following numbers:

βγ-Unsaturated acid.	$E_{\text{MeOH}}^{15^\circ}$.	Saturated acid.	$E_{\text{MeOH}}^{15^\circ}$.
βγ-Phenylcrotonic, $C_6H_5CH{:}CH \cdot CH_2 \cdot CO_2H$	86·6	*γ*-Phenyl-*n*-butyric ...	56·25
Hydrosorbic, $CH_3 \cdot CH_2 \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$.........	69·1	*n*-Hexoic	51·5 [2]
β-Phenylethylidenepropionic, $CH_2Ph \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$.....	82·1	*δ*-Phenyl-*n*-valeric ...	39·6
Ethylidenepropionic, $CH_3 \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$	74 [3]	*n*-Valeric	53·5 [2]

When the double linking is still further removed from the carboxylic group, its effect is very slight, so that there is very little difference between the constant of the unsaturated acid and that of its saturated analogue.

Unsaturated acid.	$E_{\text{MeOH}}^{15^\circ}$.	Saturated analogue	$E_{\text{MeOH}}^{15^\circ}$.
Allylacetic, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$...	45·5	*n*-Valeric..................	53·5 [2]
Cinnamenylpropionic.........................	48·7	*γ*-Phenyl-*n*-valeric......	39·6
Oleic...	54·3	Palmitic	49·7 [2]
Ellaidic	54·3		

The acids, undecylenic, $CH_2{:}CH \cdot [CH_2]_8 \cdot CO_2H$, and erucic, $CH_3 \cdot [CH_2]_9 \cdot CH{:}CH[CH_2]_9 \cdot CO_2H$, and the stereoisomeride of the latter, brassidic acid, give values between 51 and 54, which are of the order of magnitude of the constants for normal fatty acids (Trans., 1908, **93**, 211).

4. The effect of conjugate double bonds, one of which is in the

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[1] Sudborough and Roberts, *loc. cit.*

[2] Sudborough and Gittins, *loc. cit.*

[3] Sudborough and Thomas, *loc. cit.*

$\alpha\beta$-position with respect to the carboxylic group, is seen in the case of sorbic and cinnamylideneacetic acids.

Conjugate acid.	$E^{15°}_{MeOH}$.	Saturated.	$E^{15°}_{MeOH}$.
Sorbic, $CH_3 \cdot CH:CH \cdot CH:CH \cdot CO_2H$ ……	0·73	*n*-Hexoic ……………	51·5 [1]
Cinnamylideneacetic, $C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CO_2H$ ………	0·74	δ-Phenyl-*n*-valeric …	39·6

The conjugate linkings have a somewhat greater inhibiting effect than an $\alpha\beta$-double linking.

5. The relationships between the constants for *cyclo*hexanecarboxylic, benzoic, and phenylacetic acids are interesting. In benzoic acid there are conjugate double linkings, one of which is in the $\alpha\beta$-position, and when these are removed by reducing the benzoic acid to hexahydrobenzoic acid, the value of $E^{15°}_{MeOH}$ rises from 0·25 to 19·3.

The value for *cyclo*hexanecarboxylic acid is of the same order of magnitude as the dialkylated acetic acids, for example:

*cyclo*Hexanecarboxylic ………………	19·3
Dimethylacetic (*iso*butyric) …………	33·6
Methylethylacetic ……………………	12·6

When a methylene group is interposed between the benzene nucleus and the carboxylic group, as in phenylacetic acid, $C_6H_5 \cdot CH_2 \cdot CO_2H$, there is no longer a double bond in the $\alpha\beta$-position, and the constant rises to 50, a value of the same order of magnitude as those for the higher normal fatty acids.

Undoubtedly interesting results would be obtained by a study of the di- and tetra-hydrobenzoic acids from the point of view of velocity of esterification, and we hope to be able to undertake this investigation at an early date.

Some of the results we have obtained are of importance from a practical as well as from a theoretical point of view. There are various methods by means of which it is possible to determine whether, in a given unsaturated acid, the olefine linking is in the $\alpha\beta$- or $\beta\gamma$-position. The two most commonly used are: (1) An examination of the products of oxidation, and (2) an investigation of the action of moderately concentrated sulphuric acid (Fittig, *Annalen*, 1894, **283**, 51). The results which we have obtained suggest a further method, namely, a comparison of the esterification constant of the unsaturated acid with that of its reduction product (saturated analogue). If the constant for the saturated acid is of a much higher order of magnitude than that for the unsaturated acid, the presence of a double linking in the $\alpha\beta$-position is proved. The method has the advantage that, as a rule, the acid can be recovered.

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[1] Sudborough and Gittins, *loc. cit.*

Our results also indicate that the method of fractional esterification could be used with advantage in the separation of a mixture of isomeric $\alpha\beta$- and $\beta\gamma$-unsaturated acids. This method has the advantage over Fittig's, where the $\beta\gamma$-acid is always converted into a lactone, that both acids could be isolated. A similar method could also be used for the separation of a mixture of an $\alpha\beta$-unsaturated acid and its reduction product.

EXPERIMENTAL

The general method of carrying out the determinations was identical with that already described (Trans., 1899, **75**, 471): 100 c.c. of a 0·1*N*-solution of the organic acid in methyl alcohol were prepared and titrated with standard barium hydroxide solution, using phenolphthalein as indicator. The number of c.c of the alkali required to neutralise 15 c.c. of this acid solution was taken as the value for a. Seventy c.c. of this acid solution were mixed with 70 c.c. of a standard solution of hydrogen chloride in methyl alcohol, and the time noted. The mixture was well shaken, and portions of 30 c.c. run into four small bottles, which were kept in a thermostat at 15°, and titrated after given intervals of time. The number of c.c. of alkali required in each case, less the number of c.c. required for the amount of hydrogen chloride present, gave the value $a-x$. The constant K was then calculated by means of the usual equation for a unimolecular reaction, $K=1/t\log_{10}a/a-x$. To obtain comparative results, these numbers were multiplied by the concentration of the hydrogen chloride and by the factor 2·3026, and thus give the values of $E^{15^\circ}_{MeOH}$.

In all cases, two or three series of determinations were made, frequently using hydrogen chloride of different concentrations, and the values, E, given are the means of all the results obtained.

Preparation of the Acids.

γ-Phenylbutyric acid, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2H$, was prepared by reducing phenyl-$\beta\gamma$-crotonic acid with sodium amalgam. Thiele (*Annalen*, 1899, **306**, 101) has shown that $\alpha\beta$-unsaturated acids are more readily reduced than acids in which the double linking is further removed from the carboxylic group, and it is usually stated that $\beta\gamma$-unsaturated acids cannot be reduced by sodium amalgam and alkali (Fichter and Bauer, *Ber.*, 1898, **31**, 2003). Kipping and Hill (Trans., 1899, **75**, 147) state that $\beta\gamma$-phenylcrotonic acid is readily reduced by sodium amalgam at the ordinary temperature, whereas Jayne (*Annalen*, 1883, **216**, 97) states that prolonged action and a fairly high temperature are necessary. Our experiments confirm Jayne's conclusion, as we were unable to

			$1/t\log_{10}a/a-x$.			
Acid.	Series.	Conc. of hydrogen chloride.	Max.	Min.	Mean corrected for *N* HCl.	$E^{15^\circ}_{MeOH}$.
*cyclo*Hexanecarboxylic	*a*	0·006612*N*	0·0580	0·0536	8·49	19·3
	b	0·02059*N*	0·177	0·168	8·36	
	c	0·02608*N*	0·224	0·213	8·32	
Benzoic..........................	*a*	0·04372*N*	0·00484	0·00467	0·109	0·252
	b	0·05291*N*	0·00589	0·00581	0·110	
Phenylacetic	*a*	0·01241*N*	0·275	0·267	21·8	50·0
	b	0·01214*N*	0·266	0·259	21·6	
	c	0·01866*N*	0·407	0·402	21·7	
β-Phenylpropionic	*a*	0·00995*N*	0·204	0·201	20·3	47·3
	b	0·0146*N*	0·311	0·302	20·9	
	c	0·0118*N*	0·243	0·239	20·4	
γ-Phenyl-*n*-butyric............	*a*	0·0118*N*	0·295	0·286	24·7	56·3
	b	0·00661*N*	0·162	0·158	24·2	
δ-Phenyl-*n*-valeric	*a*	0·01274*N*	0·221	0·210	17·01	39·5
	b	0·01274*N*	0·226	0·213	17·27	
Furfurylpropionic	*a*	0·01093*N*	0·217	0·198	18·9	43·9
	b	0·01921*N*	0·387	0·354	19·2	
α-Phenylpropionic	*a*	0·07345*N*	0·210	0·307	4·20	9·65
	b	0·07345*N*	0·311	0·300	4·18	
α-Phenylbenzylacetic	*a*	0·03857*N*	0·0608	0·0595	1·56	3·58
	b	0·03857*N*	0·0602	0·0596	1·55	
Undecylenic........................	*a*	0·01567*N*	0·368	0·358	23·0	52·5
	b	0·01761*N*	0·405	0·387	22·6	
Oleic..	*a*	0·01561*N*	0·387	0·359	23·6	54·3
	b	0·01563*N*	0·385	0·359	23·5	
Elaidic	*a*	0·01761*N*	0·420	0·407	23·6	54·3
	b	0·01561*N*	0·382	0·364	23·7	
Erucic	*a*	0·01624*N*	0·381	0·346	22·2	52·3
	b	0·01572*N*	0·383	0·350	23·2	
Brassidic	*a*	0·01588*N*	0·364	0·345	22·5	51·6
	b	0·01628*N*	0·394	0·348	22·2	
Phenyl-βγ-crotonic	*a*	0·01147*N*	0·434	0·419	37·1	86·6
	b	0·01147*N*	0·450	0·426	38·1	
Allylacetic	*a*	0·02162*N*	0·431	0·420	19·6	45·6
	b	0·02162*N*	0·439	0·427	20·0	
Hydrosorbic	*a*	0·01133*N*	0·354	0·332	30·2	69·1
	b	0·0124*N*	0·374	0·365	29·8	
Phenylpropylideneacetic ...	*a*	0·07406*N*	0·0443	0·0421	0·577	1·33
	b	0·07578*N*	0·0461	0·0425	0·575	
Phenylethylidenepropionic .	*a*	0·01111*N*	0·411	0·380	35·5	82·0
	b	0·01037*N*	0·386	0·361	35·7	
Cinnamenylacetic	*a*	0·02424*N*	0·525	0·500	21·0	48·7
	b	0·01786*N*	0·396	0·368	21·3	
Cinnamylideneacetic	*a*	0·1814*N*	0·0587	0·0567	0·318	0·737
	b	0·0741*N*	0·0246	0·0233	0·321	
Sorbic acid	*a*	0·1454*N*	0·0466	0·0464	0·320	0·730
	b	0·1454*N*	0·0462	0·0455	0·315	
αβ-Oleic	*a*	0·1003*N*	0·0573	0·0569	0·569	1·36
	b	0·03857*N*	0·0242	0·0223	0·614	
*allo*Cinnamic	*a*	0·1003*N*	0·0387	0·0383	0·383	0·905
	b	0·1003*N*	0·0415	0·0399	0·403	
Tetrolic	*a*	0·2039*N*	0·114	0·110	0·553	1·29
	b	0·2039*N*	0·117	0·114	0·567	

bring about the reduction at the ordinary temperature. The method we finally adopted was to dissolve the unsaturated acid in a very slight excess of aqueous sodium hydroxide, and to maintain the solution at 80—90° during three days. This was accomplished by placing the solution in a separating funnel which was immersed in a hot-water bath. Some twenty times the theoretical amount of 4 per cent. sodium amalgam was introduced in small portions, the whole was well shaken from time to time, and dilute sulphuric acid added occasionally, so that the solution was never strongly alkaline. The acid was subsequently precipitated by the addition of sulphuric acid, and, after several recrystallisations from light petroleum, gave a 50 per cent. yield of nearly pure phenylbutyric acid (m. p. 47·5°).

δ-Phenyl-*n*-valeric acid, $C_6H_5\cdot[CH_2]_4\cdot CO_2H$, was prepared by reducing phenylpropylideneacetic acid (γδ-dihydrocinnamylideneacetic acid) with sodium amalgam in alkaline solution at 60—80°. The product obtained was a mixture of the reduced and original acids, which was separated by repeated crystallisation from light petroleum (b. p. 34—40°), when the saturated acid was obtained in colourless prisms, m. p. 57—58°: Baeyer (*Ber.*, 1880, **13**, 122) gives m. p. 58—59°.

The reduced cinnamylideneacetic acids were prepared by a method almost identical with that described by Riiber (*Ber.*, 1904, **37**, 3121). Cinnamylideneacetic acid was crystallised from benzene and obtained in colourless prisms, m. p. 165°.

β-Phenylethylidenepropionic acid (αδ-dihydrocinnamylideneacetic acid), $C_6H_5\cdot CH_2\cdot CH\colon CH\cdot CH_2\cdot CO_2H$, crystallises from light petroleum (b. p. 34—40°) in large, lustrous plates, m. p. 31°. Cinnamenylpropionic acid (αβ-dihydrocinnamylideneacetic acid), $C_6H_5\cdot CH\colon CH\cdot CH_2\cdot CH_2\cdot CO_2H$, also crystallises from light petroleum (b. p. 40—60°) in long, colourless plates, m. p. 91°. Phenylpropylideneacetic acid (γδ-dihydrocinnamylideneacetic acid), $C_6H_5\cdot CH_2\cdot CH_2\cdot CH\colon CH\cdot CO_2H$, crystallises from hot carbon disulphide in glistening, prismatic needles, m. p. 104°. α-Phenylbenzylacetic acid, obtained by reducing α-phenylcinnamic acid with sodium amalgam, forms colourless crystals, m. p. 88—89°. Furfurylpropionic acid, obtained by reducing furfurylacrylic acid, was crystallised from light petroleum, and melted at 57—58°. Erucic acid crystallised from light petroleum (b. p. 30—40°) in colourless plates, and melted at 33°. It was transformed into its isomeride, brassidic acid, by means of nitrous acid, and this, after recrystallisation from a mixture of chloroform and light petroleum, was obtained in mother-of-pearl plates, m. p. 59·5—60°.

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XL.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIV. Ethyl Tartrate in Benzaldehyde and in Quinoline.*

By THOMAS STEWART PATTERSON and DAVID PATERSON McDONALD, M.A., B.Sc.

IN a recent communication (Trans., 1908, **93**, 1837) attention was directed to certain regularities which had been observed in regard to the effect of temperature-change on the rotation of ethyl tartrate in solution. It was shown that whilst the homogeneous ester has a maximum rotation of +15° at 175°, a maximum rotation also occurs in media which, like nitrobenzene and α-nitronaphthalene, have a powerful elevating effect on the rotation of the tartrate. The value of this maximum rotation generally increases, and is displaced towards a lower temperature as the dilution becomes greater. Further, when the specific rotation of a solution of ethyl tartrate in any of the solvents hitherto examined is greater than about +20° at 20°, the rotation diminishes on heating.

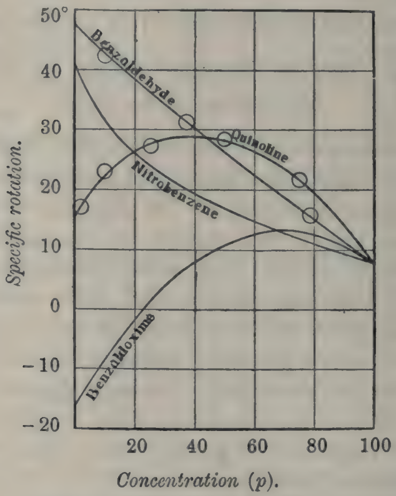
As these are perhaps the most comprehensive regularities yet observed in regard to rotation in solution, it seemed desirable to extend the investigation to include other solvents of this type. The present paper deals with two such, benzaldehyde and quinoline, both of which exhibit the behaviour described, but, in the case of quinoline, with some new and interesting modifications.

Ethyl Tartrate in Benzaldehyde.

In Fig. 1 is shown the concentration-rotation curve for benzaldehyde at 20°, and for comparison the corresponding curve for nitrobenzene is included. The two curves show some difference. The influence of benzaldehyde is, at all concentrations, greater than that of nitrobenzene, the rotation being almost a linear function of the concentration, whereas in nitrobenzene the rotation increases, on further dilution, more rapidly in dilute than in concentrated solution. The rotation at infinite dilution would be $+47{\cdot}5^\circ$, so that benzaldehyde is only inferior to α-nitronaphthalene and *o*-dinitrobenzene in its solvent influence.

As regards the effect of temperature-change, the behaviour of benzaldehyde is very much what was to be expected from the observations recorded in the last paper (Part XIII) of this series, as is shown in Fig. 2. At the concentrations $p=9{\cdot}97$ and $p=35{\cdot}5$, when the specific rotation at 20° is much above $+20^\circ$, the rotation diminishes rapidly on heating and to a greater extent in the more dilute solution, whereas at the concentration $p=78{\cdot}75$, when the specific rotation at 20° is somewhat below $+20^\circ$, the rotation increases to a slight extent. At intermediate concentrations a maximum rotation would doubtless appear.

Fig. 1.—*Concentration–Rotation curves.*



Ethyl tartrate in various solvents.

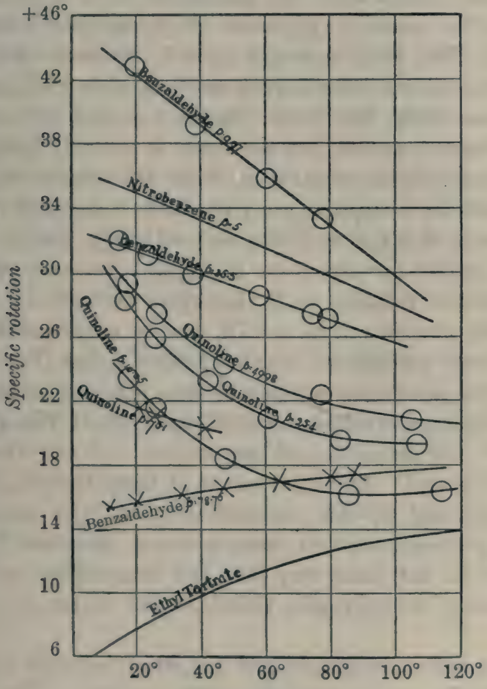
It is also interesting that the expression, $[\alpha]_D^{100^\circ} = 0{\cdot}495\,[\alpha]_D^{20^\circ} + 10{\cdot}583$, connecting the rotation at 100° with that at 20°, deduced in the previous paper from the behaviour of two nitrobenzene solutions—an expression which was shown to govern with remarkable closeness the change of rotation with alteration of temperature in a considerable number of solvents—applies also, equally satisfactorily, to the solutions in benzaldehyde.

The following table shows the agreement between the experimental and the calculated values.

p.	$[\alpha]_D^{20°}$.	$[\alpha]_D^{100°}$ (observed).	$[\alpha]_D^{100°}$ (calculated).
9·97	+42·4°	+29·7°	+31·6°
35·5	31·3	25·4	26·1
78·75	15·7	17·6	18·4

The behaviour of benzaldehyde may thus be described as normal, inasmuch as it is in agreement with the regularities observed for other solvents.

FIG. 2.—*Temperature–Rotation curves.*



Ethyl tartrate in various solvents.

Ethyl Tartrate in Quinoline.

The data for quinoline, which differ in important respects from those obtained for benzaldehyde, are represented by some of the curves in Figs. 1 and 2. In Fig. 1 the concentration-rotation curve is shown. Following the curve from right to left it will be seen that addition of quinoline to the pure ester raises the rotation of the latter much more rapidly even than nitrobenzene or benzaldehyde.

The rate of increase becomes less, however, as the proportion of quinoline increases, until at a concentration of $p=44$ the specific rotation has a maximum value of +29°. Further dilution then causes diminution of the rotation, which reaches a final value of +15·4° at infinite dilution. The curve is thus in its general character similar to that representing the variation of the specific rotation of solutions of ethyl tartrate in benz*anti*aldoxime (Trans., 1907, **91**, 508), which rises gradually to the maximum value +13·6° at $p=70$, and then rapidly falls to reach the value −16° at infinite dilution.

Other solvents also show an analogous, but much less marked, behaviour, as, for example, glycerol, ethyl alcohol, *n*-propyl alcohol (Trans., 1901, **79**, 180), *iso*butyl alcohol, *sec.*-octyl alcohol (Trans., 1901, **79**, 483), carbon tetrachloride, methylene chloride, and ethylidene chloride (Trans., 1908, **93**, 355). In these cases a minimum rotation —not a maximum—occurs, but the cause is possibly similar.

It is perhaps worth remarking that the maximum rotation is found in a mixture containing very nearly two molecules of quinoline for one molecule of ethyl tartrate, and although we do not wish to lay any very particular stress on this point, we may recall the fact that the maximum rotation at 20° for ethyl tartrate in benzaldoxime occurs at the concentration $p=70$, nearly corresponding with one molecule of ethyl tartrate and one molecule of oxime (Trans., 1907, **91**, 509), whilst the minimum rotation in glycerol at the same temperature is found at the concentration $p=68$ (Trans., 1901, **79**, 179), which is very nearly in the proportion of one molecule of ethyl tartrate to one molecule of glycerol. The significance of these facts is, however, considerably minimised by the consideration that the concentrations at which these critical rotations occur are not the same * for different temperatures, in the same way that the composition of the constant boiling mixture of hydrogen chloride and water varies with the pressure.

The concentration-rotation curve for ethyl tartrate in quinoline is thus remarkable, but is not without congeners. The temperature-rotation curves are, however, unique. The rotations of all the solutions examined, except the most dilute, have values at 20° greater than +20°. It was therefore to be expected that, on heating, the rotations should diminish, and this is, indeed, the case, but it will be noticed that the curves differ distinctly from those representing the behaviour of solutions in benzaldehyde and nitrobenzene, inasmuch as they are convex with regard to the point of origin of the figure.

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* They do not differ very much, however. In quinoline, the maximum rotation occurs at 20° at $p=44$ and at 70° at $p=50$.

Each, indeed, seems to tend towards a minimum value, which in the case of a $p = 10$ solution would lie about $+16°$ at 95°. Unfortunately we were unable definitely to ascertain whether there really is a minimum or not, since at a temperature near 130° decomposition ensued, and the solutions became too dark in colour to be examined with accuracy in the polarimeter, a fact which somewhat favours the view that in this case the rotation changes may be due to chemical combination between solvent and solute, since neither substance alone would be altered at that temperature. We may specially remark that heating of the solutions—at least up to about 120°—did not permanently alter their activity; their rotations returned to the original values on cooling.

It will be obvious from the curves in Fig. 2 that the expression quoted on p. 322 could not be applied satisfactorily in this case. It may be that the peculiar behaviour of the quinoline solutions on heating is connected with the form of the concentration-rotation curve, and that other solvents causing the same type of concentration curve and having a powerful elevating influence will have a similar temperature effect. The elucidation of this point must be left for future investigation.

EXPERIMENTAL.

Ethyl Tartrate in Benzaldehyde.

The benzaldehyde was carefully purified and was distilled under diminished pressure. The data obtained were as follows:

I. $p = 9·97$.

t°	19·9°	20°	38·8°	49·6°	60·3°	78°	100°
$\alpha_D^{t^\circ}$ (70 mm.)..	+3·18	—	2·87	2·74	2·58	2·36	—
$[\alpha]_D^{t^\circ}$	+42·8	42·4*	39·2	37·8	35·9	33·3	29·7*

II. $p = 35·5$.

t°	14·4°	20°	23·3°	37·4°	58·5°	75°	79°	100°
$\alpha_D^{t^\circ}$ (70 mm.)	+8·82	—	8·49	8·07	7·56	7·15	7·05	—
$[\alpha]_D^{t^\circ}$	+32·0	31·3*	31·01	29·85	28·5	27·36	27·08	25·4*

III. $p = 78·75$.

t°..................	20°	34·2°	47·8°	64°	81°	87·4°	100°
$\alpha_D^{t^\circ}$ (70 mm.) ...	+10·15	10·23	10·31	10·55	10·67	10·66	—
$[\alpha]_D^{t^\circ}$	+15·72	16·07	16·42	17·09	17·41	17·51	17·6*

* Interpolated or extrapolated values.

Densities Determined.

Solvent.		I.		II.		III.†	
t°.	*d*.	*t*°.	*d*.	*t*°.	*d*.	*t*°.	*d*.
18·5°	1·0517	18 05°	1·0650	17·7°	1·105	20°	1·171*
20	1·0498	20	1·0634*	20	1·1027*	60	1·125*
31·65	1·0398	21·5	1·0620	22·2	1·101		
		31·1	1·054	31·15	1·092		
		42·4	1·043				

* Interpolated or extrapolated values.

† By an oversight, the density of solution III was not determined. The density values used in calculating the specific rotation have therefore been derived by interpolation from the data for the pure solvent, for ethyl tartrate, and for the two solutions.

Ethyl Tartrate in Quinoline.

The quinoline was carefully re-distilled. It boiled at 114°/17 mm. (oil-bath at 155°).

I. p = 1·021.

t°.	$\alpha_{\rm D}^{t^\circ}$ (400 mm.).	Density.	$[\alpha]_{\rm D}^{t^\circ}$.
26°	+0·752°	1·090	+16·88°

II. p = 10·05.

t°	17·7°	20°	26°	47·5°	85·5°	114·5°
$\alpha_{\rm D}^{t^\circ}$ (160 mm.) ...	+4·184	—	3·824	3·210	2·736	2·714
$[\alpha]_{\rm D}^{t^\circ}$	+23·45	22·9*	21·55	18·38	16·13	16·38

III. p = 25·40.

t°	16·4°	20°	26°	42°	60·8°	82·5°	107°
$\alpha_{\rm D}^{t^\circ}$ (160 mm.)	+13·036	—	11·772	10·466	9·279	8·502	8·18
$[\alpha]_{\rm D}^{t^\circ}$	+28·26	27·3*	25·89	23·23	20·88	19·49	19·03

IV. p = 49 98.

t°	17·2°	20°	26°	46·9°	77°	105°	131°†
$\alpha_{\rm D}^{t^\circ}$ (75 mm.)..	+12·746	—	11·844	10·326	9·24	8·447	8·08
$[\alpha]_{\rm D}^{t^\circ}$	+29·29	28·6*	27·40	24·24	22·17	20·70	20·16

V. p = 75·10.

t°..........................	20°	21·3°	26°	41·5°
$\alpha_{\rm D}^{t^\circ}$ (75 mm.)	—	+14·33	13·972	13·18
$[\alpha]_{\rm D}^{t^\circ}$........................	+21·7‡	21·56	21·08	20·13

* Interpolated.

† At this temperature, the solution darkened, and an accurate reading was not possible. It was certain, however, that the rotation was still diminishing.

‡ Extrapolated.

Densities Determined.

II.		III.		IV.		V.	
t°.	*d.*	*t°.*	*d.*	*t°.*	*d.*	*t°.*	*d.*
19·5°	1·109	19·8°	1·1293	20·7°	1·1587	20·3°	1·181
22·5	1·107	22·6	1·1268	27·2	1·1527	28·0	1·174
27·0	1·103	25·3	1·1247	30·6	1·151		
99·0	1·044	99·0	1·060				

THE UNIVERSITY,
GLASGOW.

XLI.—*The Action of β-Rays on Photosensitive Solutions.*

By OTTO FLASCHNER.

OF the whole radiation emanating from radioactive matter, the β-rays affect the photographic plate the most. Since, however, it is impossible to measure the intensity of the effect on a photographic plate with appreciable accuracy, it seemed to be of interest to ascertain if other actinometers are affected by the β-rays, and if the magnitude of the reaction is within easily measurable limits; further, to discover if laws similar to those proved to hold by the electrometric method of measurement can be substantiated if the intensity of radiation is measured by a chemical reaction.

The present paper gives a preliminary account of the work.

The use of a silver electrode covered with a silver halide as an actinometer was first due to Becquerel (1839). More recent researches by Luggin (*Zeitsch. physikal. Chem.*, 1894, **14**, 385; 1897, **23**, 577) have extended our knowledge by showing that the sensitiveness of such an electrode is much increased by using platinum covered with silver halide previously polarised to a high potential. For instance, the potential of such an electrode when illuminated with an Argand burner (2·78 K.M^{-2}) * rises from $-0·345$ in direct proportion to the time of exposure to $-0·133$ volt, and returns to its initial value when the source of light is removed.

For the experiments forming the subject of this paper I had at my disposal radium emanation which had accumulated from a solution of radium bromide corresponding with about 0·23 gram of metallic radium. For the purpose in view, the electrode was made of such a shape that the gas could be introduced and kept on its surface. Fig. 1 gives an idea of the apparatus used. A small, round platinum disk, 1·5 sq. cm. in area and 0·002 cm. thick, was cemented to the end of the inner tube *E*. The platinum plate was electrolytically coated with 4·18 milligrams of silver, which was then converted into silver bromide. The electrode was afterwards thoroughly washed. From the platinum plate a platinum wire led downwards and projected through the tube. In this way it was possible to measure the potential of the electrode from the outside. The space below the electrode could be evacuated, while the tap *I* was opened so as to make the pressure on both sides of the platinum plate nearly equal. The space above the electrode was filled with 0·1*N*-solution of potassium bromide. This solution was supplied from the reservoir *S*, and it communicated with a 0·1*N*-calomel electrode, which is the negative pole of the cell. The emanation, mixed with about 1 c.c. of any gas other than hydrogen, and passed into the apparatus through the inverted siphon, was forced up by raising the mercury in *R*. The outside of the electrode was protected against the action of light by means of black paper. The method of measuring was the compensation method, using a Dolezalek electrometer as a null-instrument.

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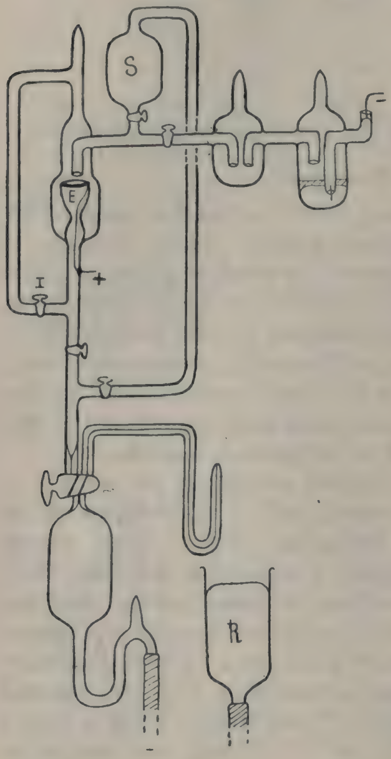
* That is, the illumination being 2·7 candle-power per sq. metre.

FIG. 1.



Experiment I.—The emanation had accumulated for twenty-two hours, and was mixed with 1 c.c. of oxygen. The following table shows the increase of the positive potential with time expressed in minutes. It may be mentioned that the potential was observed one day before starting the experiment, and proved constant within 0·004 volt.

TABLE I.

Volt.	Minutes.
0·203	0
0·199	4
0·214	27
0·215	75
0·227	215
0·461	1320
0·521	1850
0·559	2750
0·564	2910
0·561	3220
0·600	4270
0·651	5700
0·653	7080
0·653	8610
0·653	10030
0·647	11790
0·428	17370
0·053	56500

From these numbers it is surprising to see that the increase of potential is not linear; the maximum is reached slowly, and persists for a long time; then the potential falls below its initial value.

Experiment II.—The same electrode was used for this experiment after the potential raised by the first introduction of emanation had sunk to a low value. The emanation had accumulated for twenty-one hours, and was mixed with 1 c.c. of nitrogen.

TABLE II.

Volt.	Minutes.	Volt.	Minutes.
0·080	0	0·141	5610
0·075	240	0·142	6000
0·154	1310	0·131	7020
0·148	1740	0·130	8880
0·146	2760	0·110	10080
0·133	4290	0·069	21480

The maximum was obtained in a shorter time than in the first experiment. The conclusions to be drawn from these two experiments are:

(1) The potential of an AgBr/KBr electrode is changed under the influence of β-rays in the same direction as it would be by the action of light.

(2) The higher the initial potential the more sensitive is the electrode to β-rays, just as in the case of light.

The Eder's actinometer (*Sitzungsber. K. Akad. wiss. Wien*, 1879, **2**, 636) was chosen as a second type of a reaction which is influenced by light. This is represented by the approximate equation: $2HgCl_2 + C_2O_4(NH_4)_2 = Hg_2Cl_2 + 2NH_4Cl + 2CO_2$. The latest work on this subject has been done by Roloff (*Zeitsch. physikal. Chem.*, 1894, **13**, 329), who showed that an increase of the oxalic and mercuric ions produced an acceleration of the reaction. Consequently the light-reaction can be regarded as a catalysis of

$$2Hg^{\cdot\cdot} + C_2O_4'' = 2Hg^{\cdot} + 2CO_2.$$

From this result, and from the results of two other light-reactions which he examined, Roloff concluded that reactions influenced by light consist in a transport of electric charge, and that the action of light has an accelerating influence on the transport. "If the electric charge of an ion has a tendency to pass into a more stable condition or to another atom, where it is in a more stable condition, it is evident that this transport is accelerated by certain electrical vibrations due to light."

From these conclusions it was very probable that β-rays would affect the same reaction. Becquerel (*Compt. rend.*, 1901, **133**, 709) has already stated that this reaction takes place under the influence of radium radiations. To ascertain the kind of rays to which this reaction is due, a box of paraffin was made and divided by very thin glass sheets into five separate cells. The depth of each cell was about 2·5 cm., and its capacity was 25 c.c. The box was filled with the Eder's solution and placed outside a bulb which contained a solution of radium bromide, so that the rays could pass through all the cells one after the other.

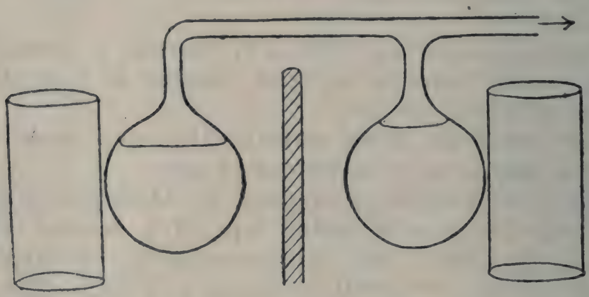
The weight of mercurous chloride precipitated was as follows:

In cell No.	1.	0·0806 gram.
,,	2.	0·0515 ,,
,,	3.	0·0384 ,,
,,	4.	0·0300 ,,
,,	5.	0·0054 ,,

It is evident from these numbers that the acceleration of the reaction is chiefly due to β-rays.

It would be of interest to see how the strength of β-rays measured by this reaction is diminished by interposition of metallic sheets. Further, the connexion between the velocity of the β-rays and chemical action seems to be interesting. A quantitative comparison between the actinometric effect of light and of a constant source of β-rays remains to be investigated.

FIG. 2.



Attention may here be drawn to a curious observation. Two glass bulbs (Fig. 2), both containing solutions of radium bromide—the first 0·05 gram and the second 0·497 gram—were connected to a pump and evacuated. The β-rays between these bulbs were cut off by means of a lead screen 3 mm. thick. Outside both bulbs were placed tubes containing 75 c.c. of Eder's solution. It might have been expected that the bulb containing 0·497 gram of radium bromide would have had about ten times the effect of the other, which contained only 0·05 gram. It was surprising to notice that the tube beside the latter yielded a precipitate of 0·2863 gram of mercurous chloride during twenty-four days, whilst the one beside the former contained a precipitate of only 0·2254 gram accumulated in the same time. An explanation would be that the amount of water in both bulbs was nearly the same—slightly more in that containing 0·05 gram—so that the emanation distilled over and was divided between the two bulbs according to the water present.

From the facts noted it appears evident that there is a similarity between the chemical effect of light and that of β-rays.

I hope shortly to extend this investigation to other photochemical processes, including the assimilation of plants.

I take the opportunity of expressing my thanks to Sir William Ramsay for his help and advice, as well as for the kind way in which he placed the radioactive preparations at my disposal.

UNIVERSITY COLLEGE,
LONDON.

XLII.—*The Effect of Contiguous Unsaturated Groups on Optical Activity. Part I.*

By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

A CONSIDERABLE time has elapsed since the anomalous chemical behaviour of two contiguous ethylenic linkings was first remarked, notably by Fittig (*Annalen*, 1872, **161**, 309, etc.), Baeyer (*Annalen*, 1889, **251**, 278, etc.), and others working on reactions such as the addition of hydrogen to compounds containing this unsaturated system. The explanation put forward by J. Thiele (*Annalen*, 1899, **306**, 87), that the affinities of the carbon atoms are not completely utilised in the formation of a double bond, and that, therefore, each atom in the system is left with a residue of affinity (a "partial valency"), served to adapt the accepted statical views of chemical structure to the observed facts in this and several other cases, such as the addition of sodium hydrogen sulphite to carbonyl compounds containing the nucleus ·CH⁚CH·CO·, when (by addition to the ethylenic bond) the sodium salt of a ketonic hydrosulphonic acid, and not the usual "bisulphite compound," is formed (Pinner, *Ber.*, 1883, **16**, 1727; Ludwig, *Monatsh.*, 1888, **9**, 658; Knoevenagel, *Ber.*, 1904, **37**, 4038).

The irregularities shown by these compounds in chemical behaviour also extend to various physical properties, for in cases where it is possible to estimate the numerical value of the property in question, it is found that discrepancies exist between the calculated and observed figures for substances containing adjacent unsaturated groups. For instance, the refractive index of such compounds is usually abnormally large (Brühl, *Ber.*, 1907, **40**, 881, 1157), and Sir W. H. Perkin observed similar anomalies in magnetic rotatory power (Trans., 1907, **91**, 806). The present work extends the examination of the physical properties of these groups to optical activity, in order to inquire if similar abnormal behaviour exists here; the rotatory power of optically active compounds which possess a system of contiguous unsaturated groups has been observed to be abnormal in several isolated instances, but a systematic study of the effect of the various different combinations of adjacent unsaturated groups does not appear yet to have been undertaken. The author is at present engaged in the examination of several such series, and it is hoped to publish data in subsequent papers relating to the molecular rotatory power of optically active substances containing carbonyl, carboxyl, benzenoid, ethenoid, or other unsaturated radicles in adjacent positions to each other, and so to obtain a conception of the precise effect of different types of conjugated unsaturation on this somewhat complex physical property. The results now presented deal chiefly with the effect of interposing a relatively saturated group between the asymmetric atom and the system of contiguous unsaturated groups, whilst at the same time the influence of carbonyl and ethylenic groups in conjunction with the benzenoid residue is discussed.

From the general susceptibility of optical activity to constitutive changes, it might be expected that even greater irregularities than those noticed in the other optical properties would be manifested, but molecular rotatory power is influenced by so many factors that it is necessary to examine a wide range of instances before reaching a satisfactory generalisation. For example, Guye, Tschugaeff, and others have shown that, other things being equal, an alteration of mass frequently has but a small effect, whilst a change in constitution may, or may not, produce a large change in optical activity; on the other hand, the same alteration in constitution has been observed to give rise to different effects in optical rotatory power in different series of compounds (compare Trans., 1908, **93**, 714). These irregularities are probably due to:

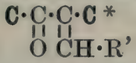
(1) Influence exerted by other (at present unrecognised) factors, which, acting on the physical property of matter to which optical activity is ultimately due, are sometimes strong enough to mask the effect of the studied change in constitution.

(2) Influences due to the spacial configuration of the molecule. In the majority of cases the latter cannot be defined with any

degree of certainty, and therefore there is no absolute criterion of the remoteness or nearness of any given group to an "asymmetric" atom, unless they are directly united to each other.

(3) The alteration in optical activity produced in each asymmetric residue (in the case of compounds containing two or more asymmetric atoms). The total effect may thus be made up of the algebraic sum of the effects produced in each asymmetric atom, and will be increased or lessened according to whether each individual residue is affected in the same or in contrary sense.

An example, in which two contiguous unsaturated groups are directly united to two asymmetric atoms, and produce a very marked increase in activity, is afforded by the condensation products of aromatic aldehydes with ketones containing the system



$$\mathbf{C}\cdot\underset{O}{\underset{\|}{C}}\cdot\underset{CH\cdot R'}{\underset{\|}{C}}\cdot\mathbf{C}\ *$$

examined by Haller (*Compt. rend.*, 1899, **128**, 1370; **129**, 1005, etc.):

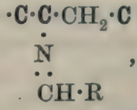
	$[M]_D$.
Benzylidenecamphor	+1020·3
Benzylcamphor	348·5
Hexahydrobenzylidenecamphor	323·9
Hexahydrobenzylcamphor	136·8
Camphor	67·2

Several other instances show that this is a general phenomenon in the camphor series:

	$[M]_D$.		$[M]_D$.
Piperonylidenecamphor	+1236·5	Piperonylcamphor	+382·5
Cuminylidenecamphor	1397·8	Cuminylcamphor	253·5
Benzylidenethujone	1416·3	Thujone	113·2
Piperonylidenethujone	2172·6		

The increased anomaly of the thujone compounds may be due to the fact that one of the asymmetric atoms in thujone is also attached to a trimethylene ring system, which is known to behave as an unsaturated group. The introduction of more unsaturated groups into the benzylidene residue, on the other hand, does not lead to further exaltation (Rupe and Frisell, *Ber*., 1905, **38**, 104):

	$[M]_D$.
Cinnamylidenecamphor	+787·7
γ-Phenylpropylcamphor	177·8

Again, bornylamine derivatives of the type  $\cdot\mathbf{C}\cdot\underset{\underset{\underset{CH\cdot R}{\|}}{N}}{\underset{|}{\mathbf{C}}}\cdot CH_2\cdot\mathbf{C}$, which possess a different asymmetric system from that mentioned above, and in which the unsaturated system is directly attached to one only of the three optically active atoms, show an entirely different effect (Forster, Trans., 1900, **75**, 1149); this may be further occasioned by the nitrogen atom interposed between the asymmetric and conjugated systems, the results given in the present paper indicating that a nitrogen or sexavalent sulphur atom so placed prevents in a large degree the exhibition of any characteristic effect by the unsaturated groups:

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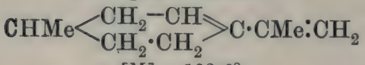
* Throughout this paper, asymmetric atoms are indicated by heavy type.

	$[M]_D$.
Bornylamine	+69·6
Benzylidenebornylamine	150·9
Benzylbornylamine	184·0

When terpene compounds containing adjacent and separated double linkings, and possessing exactly the same system of asymmetric arbon atoms, are compared, it is seen that the conjugated derivative possesses a molecular rotation usually markedly greater than that of the corresponding unconjugated derivative. The following instances may be selected to show this:

CONJUGATED.

$\Delta^{3:8(9)}$-*p*-Menthadiene.



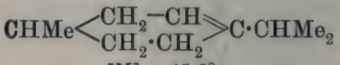
$$\mathrm{CHMe}\Big\langle\begin{matrix}\mathrm{CH_2-CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big\rangle\mathrm{C\cdot CMe{:}CH_2}$$

$[M]_D+133·6°$.

(Kay and Perkin, Trans., 1906, **89**, 839.)

UNCONJUGATED.

Menthene.

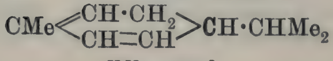


$$\mathrm{CHMe}\Big\langle\begin{matrix}\mathrm{CH_2-CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big\rangle\mathrm{C\cdot CHMe_2}$$

$[M]_D+45·2°$.

(Urban and Kremers, *Amer. Chem. J.*, 1894, **16**, 397.)

Phellandrene.

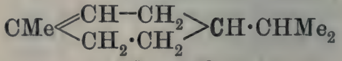


$$\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CH\cdot CH_2}\\ \mathrm{CH{=}CH}\end{matrix}\Big\rangle\mathrm{CH\cdot CHMe_2}$$

$[M]_D+82·1°$.

(Gildemeister and Stephan, *Arch. Pharm.*, 1897, **235**, 591.)

Carvomenthene.

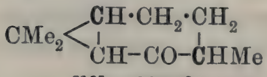


$$\mathrm{CMe}\Big\langle\begin{matrix}\mathrm{CH-CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\Big\rangle\mathrm{CH\cdot CHMe_2}$$

$[M]_D-2·9°$.

(Kondakoff and Lutschinin, *J. pr. Chem.*, 1899, [ii], **60**, 275.)

Carone.

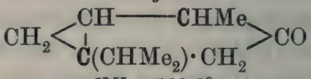


$$\mathrm{CMe_2}\Big\langle\begin{matrix}\mathrm{CH\cdot CH_2\cdot CH_2}\\ |\qquad\quad\;\; |\\ \mathrm{CH-CO-CHMe}\end{matrix}$$

$[M]_D+262·6°$.

(Baeyer, *Ber.*, 1895, **28**, 639.)

Thujone.



$$\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{CH\text{———}CHMe}\\ |\\ \mathrm{C(CHMe_2)\cdot CH_2}\end{matrix}\Big\rangle\mathrm{CO}$$

$[M]_D+113·2°$.

(Haller, *loc. cit.*)

In the last case, one of the conjugated groups is represented by the trimethylene ring complex, which, as already stated, behaves similarly to an ethylenic linking in other physical properties, such as molecular refractivity.

Klages and Sautter (*Ber.*, 1904, **37**, 649; 1905, **38**, 2312) have described some optically active benzene hydrocarbons which incidentally give prominence to the exaltation produced by contiguous benzenoid and ethenoid groups when in immediate proximity to an asymmetric atom, thus:

$CHPh:CH{\cdot}CHMeEt.$	$[M]_D.$
α-Phenyl-γ-methyl-Δ^a-pentene	+68·8°
α-*p*-*iso*Propylphenyl-γ-methyl-Δ^a-pentene	171·1
α-*p*-Ethoxyphenyl-γ-methyl-Δ^a-pentene	170·6

$CH_2Ph{\cdot}CH_2{\cdot}CHMeEt.$	$[M]_D.$
α-Phenyl-γ-methylpentane	+27·9°
α-*p*-*iso*Propylphenyl-γ-methylpentane	66·3
α-*p*-Ethoxyphenyl-γ-methylpentane	63·7

The author has previously remarked (Trans., 1908, **93**, 1388) that alkaloid salts of aromatic acids containing adjacent unsaturated groups also show enhanced optical activity, although multiple conjugation does not always produce continued exaltation. For instance:

	$[M]_D.$	Difference.
* "Normal" value for a brucine salt	−249·5°	—
Brucine benzoate	−131·1	118·4
,, anthranilate	−47·8	201·7
,, acetylanthranilate	+29·8	279·3
,, benzoylanthranilate	+156·2	405·7

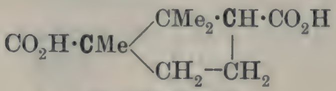
* That is, the mean molecular rotatory power of the series of salts or esters from acetic to *n*-hexoic acid.

A very striking example, showing at once the minute effect of substitution of normal groups of widely different weight at a point relatively distant from the active atoms, and also the influence of contiguous unsaturated groups near to the latter, is afforded by the diethyl and ethyl octyl esters of tartaric, diacetyl- and dibenzoyltartaric acids (McCrae, Trans., 1901, **79**, 1106):

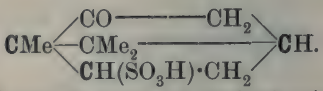
	Diethyl ester.		Ethyl octyl ester.	
Acid.	$[M]_D.$	Difference.	$[M]_D.$	Difference.
Tartaric	+15·8°	—	+22·6°	—
Diacetyltartaric	+9·9	5·9	+15·8	6·8
Dibenzoyltartaric	−247·1	262·9	−245·8	268·4

The carbonyl residue alone produces a slight increase, which is much heightened by conjugation with an aromatic nucleus. Similarly, active esters of the normal fatty acids attain an almost constant value for the molecular rotation, whereas benzoates and phenylacetates are abnormal (Guye and Chavanne, *Bull. Soc. chim.*, 1896, [iii], **15**, 277; Welt, *Ann. Chim. Phys.*, 1895, [vii], **6**, 115; Tschugaeff, *Ber.*, 1898, **31**, 360, 1775). These results, together with Rupe's work on the reduced benzoic and the isomeric unsaturated pentenoic and hexenoic menthyl esters (*Annalen*, 1903, **327**, 157), have led to the latter author's suggestion that it is in the main the nearness of the unsaturated group to the asymmetric system which determines the extent of the anomaly, phenyl and ethenoid groups possessing particularly strong effects. It appears to the author, however, that the reason depends at least as much on the proximity of the unsaturated nucleus to the carboxyl group as well as to the asymmetric system, or, in other words, on the degree of conjugation together with the nearness of the entire conjugated system to the asymmetric part of the molecule; it is hoped to deal with this point in detail in a later communication.

Two parallel series of compounds have been utilised in the present work, namely, the camphoric acid and camphor-β-sulphonic acid derivatives of certain aromatic hydroxylic and amino-compounds. As will be gathered from the formulæ, in the former case the aromatic complex is directly connected through a carboxyl group to an asymmetric carbon atom, whilst in the latter the more saturated sulphonic residue is interposed :



Camphoric acid.



Reychler's camphor-β-sulphonic acid.

EXPERIMENTAL.

The aryl hydrogen camphorates examined were prepared by a modification of a method described by Schryver (Trans., 1899, **75**, 666); the exact amount of sodium was dissolved in as slight an excess as possible of absolute alcohol, and the solution heated on the water-bath until nearly solid. The proportionate amount of the phenol, dissolved in about ten times its weight of xylene, was then added, and the whole well stirred, when the gelatinous sodium salt separated out. A very small excess of camphoric anhydride was next added, the whole maintained at about 70—80° for an hour, and then kept for a couple of hours. On extracting with an equal bulk of water, the sodium salt of the acid aryl ester dissolved, and was isolated by dilute sulphuric acid and extraction with ether. On leaving the residue from the evaporation of the dried ethereal solution in a vacuum desiccator for a few hours, it usually solidified without difficulty.

Eugenyl Hydrogen Camphorate,

$$CO_2H\cdot C_8H_{14}\cdot CO_2\cdot C_6H_3(CH_2\cdot CH{:}CH_2)\cdot OMe.$$

—This substance crystallises in colourless tablets from a mixture of light petroleum and benzene, and melts at 115° (compare Schryver, *loc. cit.*):

0·1472 gave 0·3720 CO_2 and 0·1000 H_2O. C = 68·92 ; H = 7·55.

$C_{20}H_{26}O_5$ requires C = 69·36 ; H = 7·52 per cent.

iso*Eugenyl Hydrogen Camphorate,*

$CO_2H\cdot C_8H_{14}\cdot CO_2\cdot C_6H_3(CH\colon CHMe)\cdot OMe$.

—Obtained as a white, crystalline powder from a mixture of two parts of light petroleum and one of benzene. The substance, which displayed a tendency to separate in the amorphous condition, melted at 133—135°:

0·1132 gave 0·2876 CO_2 and 0·0782 H_2O. C = 69·28 ; H = 7·68.

$C_{20}H_{26}O_5$ requires C = 69·36 ; H = 7·52 per cent.

o-*Tolyl Hydrogen Camphorate*, $CO_2H\cdot C_8H_{14}\cdot CO_2\cdot C_6H_4Me$.—Colourless, waxy leaflets, readily soluble in alcohol, benzene, or chloroform, sparingly so in light petroleum, melting at 102°:

0·1287 gave 0·3288 CO_2 and 0·0876 H_2O. C = 69·68 ; H = 7·56.

$C_{17}H_{22}O_4$ requires C = 70·34 ; H = 7·59 per cent.

o-*Aldehydophenyl Hydrogen Camphorate,*

$CO_2H\cdot C_8H_{14}\cdot CO_2\cdot C_6H_4\cdot CHO$.

—Hard, white needles, very soluble in alcohol or chloroform, sparingly so in benzene, and insoluble in light petroleum. The ester melted and decomposed slightly, at 168°:

0·1000 gave 0·2459 CO_2 and 0·0586 H_2O. C = 67·07 ; H = 6·51.

$C_{17}H_{20}O_5$ requires C = 67·10 ; H = 6·58 per cent.

The neutral camphorates of the amino-compounds were directly measured in the polarimeter by mixing the exact amounts of the constituents in chloroform and making up to the required concentration. The salts were recovered from the chloroform by evaporation, and recrystallised for analysis from dilute alcohol.

Di-p-*toluidine Camphorate*, $C_8H_{14}(CO_2\cdot C_7H_9N)_2$.—White, prismatic crystals, readily soluble in alcohol, acetone, or chloroform, melting at 172° -

0·1067 gave 0·2722 CO_2 and 0·0793 H_2O. C = 69·56 ; H = 8·26.

$C_{24}H_{34}O_4N_2$ requires C = 69·56 ; H = 8·21 per cent.

Di-p-*aminoacetophenone Camphorate*, $C_8H_{14}[CO_2\cdot C_6H_4(NH_2)\cdot COMe]_2$. —White tablets, fairly soluble in alcohol or acetone, melting at 108°:

0·1200 gave 0·2779 CO_2 and 0·0806 H_2O. C = 63·16 ; H = 7·46.

$C_{26}H_{34}O_6N_2,1\frac{1}{2}H_2O$ requires C = 62·77 ; H = 7·44 per cent.

Di-p-*aminobenzophenone Camphorate,*

$C_8H_{14}[CO_2\cdot C_6H_4(NH_2)\cdot COPh]_2$.

—White leaflets, resembling the last in solubility, melting at 116°:

0·1093 gave 0·2900 CO_2 and 0·0678 H_2O. C = 72·36 ; H = 6·89.

$C_{36}H_{38}O_6N_2$ requires C = 72·73 ; H = 6·40 per cent.

The camphor-β-sulphonates of the phenols were prepared by dissolving 5 grams of the phenol in dilute aqueous sodium hydroxide, and heating with 5 grams of camphor-β-sulphonyl chloride on the water-bath for an hour with constant shaking. The oily product was allowed to settle, and, after decanting the alkaline liquid, washed by decantation, first with more dilute aqueous sodium hydroxide, then with water, until the washings were neutral. The residue was extracted with ether, the extract dried and evaporated, and, as a rule, the product was then crystallised from a mixture of benzene and light petroleum.

Eugenyl Camphor-β-sulphonate,

$C_{10}H_{15}O{\cdot}SO_3{\cdot}C_6H_3(CH_2{\cdot}CH{:}CH_2){\cdot}OMe$.

—This substance solidified at about − 10° to white, waxy crystals, but at the ordinary temperature it was an oil. After purification as described, the last traces of solvent were removed by heating in a vacuum at 100° before using the compound for polarimetric work:

0·1582 gave 0·3704 CO_2 and 0·0926 H_2O. C = 63·86; H = 6·50.
$C_{20}H_{26}O_5S$ requires C = 63·49; H = 6·88 per cent.

iso*Eugenyl Camphor-β-sulphonate*,

$C_{10}H_{15}O{\cdot}SO_3{\cdot}C_6H_3(CH{:}CHMe){\cdot}OMe$.

—Small leaflets from a mixture of light petroleum and benzene, melting at 112—113°:

0·1082 gave 0·2536 CO_2 and 0·0651 H_2O. C = 63·92; H = 6·69.
$C_{20}H_{26}O_5S$ requires C = 63·49; H = 6·88 per cent.

o-*Tolyl Camphor-β-sulphonate*, $C_{10}H_{15}O{\cdot}SO_3{\cdot}C_6H_4Me$.—An oil which solidified to large, colourless, rhombic prisms melting at 58°:

0·1532 gave 0·3564 CO_2 and 0·0962 H_2O. C = 63·42; H = 6·98.
$C_{17}H_{22}O_4S$ requires C = 63·34; H = 6·83 per cent.

o-*Aldehydophenyl Camphor-β-sulphonate*, $C_{10}H_{15}O{\cdot}SO_3{\cdot}C_6H_4{\cdot}CHO$.—Small, white prisms, moderately soluble in alcohol or chloroform, melting at 123°:

0·1681 gave 0·3762 CO_2 and 0·0903 H_2O. C = 61·02; H 5·97.
$C_{17}H_{20}O_5S$ requires C = 60·71; H = 5·95 per cent

The camphor-β-sulphonyl derivatives of the amines were finally prepared by simply heating the amine and camphor-β-sulphonyl chloride for some time on the water-bath, as it was found that in the presence of pyridine in the cold, deeply coloured by-products resulted, making purification difficult. The compounds were usually crystallised from benzene, sometimes from alcohol. It may be mentioned here that the corresponding derivatives of *p*-aminobenzaldehyde and *p*-aminobenzaldoxime were also investigated, but were found to be of indefinite character and unsuitable for the end in view.

*Camphor-β-sulphonyl-*p*-toluidide*, $C_{10}H_{15}O{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4Me$.—White, glancing leaflets, soluble in chloroform, alcohol, or benzene, but not in light petroleum, and melting at 141°:

0·1071 gave 0·2507 CO_2 and 0·0687 H_2O. C = 63·83 ; H = 7·13.
$C_{17}H_{23}O_3NS$ requires C = 63·56 ; H = 7·16 per cent.

*Camphor-β-sulphonyl-*p-*acetylanilide*,
$C_{10}H_{15}O\cdot SO_2\cdot NH\cdot C_6H_4\cdot COMe$.
—Small, white crystals from benzene, melting at 157 :

0·1454 gave 0·3336 CO_2 and 0·0829 H_2O. C = 62·57 ; H = 6·34.
$C_{18}H_{23}O_4NS$ requires C = 61·90 ; H = 6·59 per cent.

*Camphor-β-sulphonyl-*p-*ethylphenylamide*, $C_{10}H_{15}O\cdot SO_2\cdot NH\cdot C_6H_4Et$.
—Small plates from light petroleum, melting at 117° :

0·1316 gave 0·3096 CO_2 and 0·0892 H_2O. C = 64·16 ; H = 7·53.
$C_{18}H_{25}O_3NS$ requires C = 64·48 ; H = 7·46 per cent.

*Camphor-β-sulphonyl-*p-*benzoylanilide*,
$C_{10}H_{15}O\cdot SO_2\cdot NH\cdot C_6H_4\cdot COPh$.
—Small, stout, pale yellow tablets from hot alcohol, melting at 168° :

0·1426 gave 0·3500 CO_2 and 0·0832 H_2O. C = 66·94 ; H = 6·48.
$C_{23}H_{25}O_4NS$ requires C = 67·16 ; H = 6·08 per cent.

The unsaturated systems studied may be thus classified :

I. *Contiguous Phenyl and Ethenoid Groups.*—Derivatives of eugenol and *iso*eugenol.

II. *Contiguous Phenyl and Carbonyl Groups.*—(*a*) Phenolic derivatives ; (*b*) amino-derivatives.

The measurements of the rotatory power were conducted, as in previous investigations, in dry chloroform solution at two concentrations ; the length of the polarimeter tube was always 2-dcm., and the temperature, except where otherwise stated, was 21°.

I. *Derivatives of Eugenol*, $OMe\cdot C_6H_3(OH)\cdot CH_2\cdot CH:CH_2$, *and* iso-*Eugenol*, $OMe\cdot C_6H_3(OH)\cdot CH:CHMe$.

	Percentage Concentration :					
	5			2½		
	$[\alpha]_D$.	$[M]_D$.	Diff.	$[\alpha]_D$.	$[M]_D$.	Diff.
Camphoric acid	+46·0	+92·0	—	+46·4	+92·8	—
Eugenyl hydrogen camphorate	32·7*	113·2	21·2	32·0*	110·8	18·0
*iso*Eugenyl ,, ,,	38·6*	133·6	41·6	38·0*	131·5	38·7
Camphor-β-sulphonic acid	—	+49·0	—	—	+49·0	—
Eugenyl camphor-β-sulphonate	+27·8	105·1	56·1	+28·4	107·4	58·4
*iso*Eugenyl ,,	27·6	104·3	55·3	26·4	99·8	50·8

* Temperature 23°.

II. (a) *Derivatives of* o-*Cresol*, $C_6H_4Me{\cdot}OH$, *and Salicylaldehyde*, $OH{\cdot}C_6H_4{\cdot}CHO$.

	Percentage Concentration: 5			2½		
	$[\alpha]_D$.	$[M]_D$.	Diff.	$[\alpha]_D$.	$[M]_D$.	Diff.
o-Tolyl hydrogen camphorate	+45·2	+131·1	39·1	+45·0	+130·5	37·7
o-Aldehydophenyl hydrogen camphorate	49·0	148·9	56·9	48·1	146·2	53·4
o-Tolyl camphor-*β*-sulphonate	+45·8	+147·5	98·5	+46·0	+148·1	99·1
o-Aldehydophenyl camphor-*β*-sulphonate	38·8	130·4	81·4	39·6	133·1	84·1

II. (b) *Derivatives of* p-*Toluidine*, p-*Aminoethylbenzene*, p-*Aminoacetophenone*, *and* p-*Aminobenzophenone*.

	Percentage Concentration: 5			2½		
	$[\alpha]_D$.	$[M]_D$.	Diff.	$[\alpha]_D$.	$[M]_D$.	Diff.
Di-*p*-toluidine camphorate	+22·9	+94·8	−2·8	+24·0	+99·4	−6·6
Di-*p*-aminoacetophenone camphorate	19·2	90·2	−1·8	19·4	91·2	−1·6
Di-*p*-aminobenzophenone camphorate	12·2	72·5	19·5	12·4	73·6	19·2
Camphor-*β*-sulphonyl-*p*-toluidide	68·3	219·2	170·2	71·2	228·6	179·6
Camphor-*β*-sulphonyl-*p*-ethylphenylamide	63·6	213·0	164·0	63·8	213·7	164·7
Camphor-*β*-sulphonyl-*p*-acetylanilide	67·2*	234·5	185·5	67·0*	233·8	184·8
Camphor-*β*-sulphonyl-*p*-benzoylanilide	57·1	234·7	185·7	55·6	228·5	179·5

* Temperature 23°.

With the phenolic substances, then, the camphorates show a marked rise in activity when conjugation of carbonyl or ethylenic group with the phenyl residue occurs, but the camphor-*β*-sulphonates give in one instance no definite difference, whilst in the other, the order is reversed; with the amino-compounds, the differences are only well-marked in the benzophenone derivatives, in which there exist three adjacent unsaturated nuclei. It seems natural to regard the small, indefinite change of molecular rotatory power as being the result of the interposition of the sulphone group of the camphor-*β*-sulphonic acid between conjugated system and asymmetric complex. Furthermore, the amino-group appears to exercise a similar effect. When, however, there is no such relatively saturated group between these two parts of the molecule, the compounds examined help to confirm the rule that conjugation is accompanied by a consistent increase in optical activity.

In conclusion, it may be asked if the original theory of Thiele is capable of being adapted to the explanation of the physical effects of conjugation. It is true that in many of the instances examined, the contiguous unsaturated systems can be arranged so as to form a series of neutralised "partial valencies"; this, of course, means that the effect of conjugation is ascribed to some peculiarity of the system of "neutralised" valencies referred to, and is not an ultimate explanation of the phenomena. It would here be necessary for such groups to be in actual chemical union, but instances in which unsaturated groups not directly united, but spacially near each other, also produce abnormal effects have recently been examined. The ultimate physical cause, then, of the abnormal effects of conjugation must be some property of unsaturated groups which comes into play by virtue of their nearness in space; it is not, however, possible further to discuss at present the nature of this property. The results arrived at in this paper may be summarised as follows:

(1) The contiguity of unsaturated groups produces abnormal effects on optical rotatory power.

(2) The effect is at a maximum when the conjugated system is nearest to the asymmetric carbon atom or atoms.

(3) The effect is lessened as the proximity of the unsaturated groups to one another is lessened.

(4) The effect is much decreased by the interposition of a saturated group between the conjugated and asymmetric systems.

(5) Multiple conjugation does not always lead to an increased effect.

The author desires most heartily to thank Prof. Collie, in whose laboratory most of the above work was undertaken, and further to express his indebtedness to the Research Fund Committee of the Chemical Society for a grant which has helped to meet the expenses incurred.

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XLIII.—*The Isolation of the Aromatic Sulphinic Acids.*

By John Thomas, B.Sc.

The aromatic sulphinic acids can now be easily prepared by Gattermann's method (*Ber.*, 1899, **32**, 1140), which consists in saturating a solution of the corresponding diazo-compound, as ordinarily obtained in presence of sulphuric acid, with sulphur dioxide and adding precipitated copper in the cold; evolution of nitrogen occurs, and the sulphinic acid remains partly in the solution and partly mixed with the excess of copper used. Primary aromatic amino-compounds can be converted into the corresponding sulphinic acids with almost quantitative yields by this method, which therefore affords a satisfactory one for replacing the group $-NH_2$ by the sulphinic radicle, $-SO\cdot OH$. The separation of the sulphinic acid from the solution and the copper residue is generally effected by extraction with ether, and this part of the operation is not very convenient to apply on the large laboratory scale for preparative purposes.

Since it is desirable to simplify the latter part of the laboratory method of preparing the sulphinic acids by some improvement of the method of separating them from the solution in which they are formed, Prof. W. J. Pope suggested that I should study the conditions under which the ferric salts of the sulphinic acids are deposited from solution. It was then found that all the sulphinic acids prepared are precipitated quantitatively as ferric salts from strongly acid solutions on addition of ferric chloride; the ferric salts form orange-coloured precipitates, which are readily filtered and washed, and are quite stable in dry air. The sulphinic acids, as a class, are thus characterised by this property of yielding orange-yellow ferric salts, which are insoluble in water and in fairly strong mineral acids. The ferric salts are decomposed by alkalis, giving ferric hydroxide and a solution of the alkali sulphinate, from which the free sulphinic acid can be precipitated by the addition of concentrated hydrochloric acid. On treating the solution of the sulphinic acid in sodium carbonate with sodium hypochlorite, the corresponding sulphonyl chloride is obtained, and if the ferric salt is decomposed by ammonia and then treated with hypochlorite, the corresponding sulphonamide results.

The combination of Gattermann's method of preparing the sulphinic acids with the method of separating the acids from solution as their ferric salts, leads to very simple methods for replacing the group $-NH_2$ in an aromatic amino-compound by the radicles $-SO\cdot OH$, $-SO_2Cl$, and $-SO_2\cdot NH_2$.

Ferric Benzenesulphinate, $(C_6H_5\cdot SO\cdot O)_3Fe$.

After diazotising aniline in sulphuric acid solution, saturating with sulphur dioxide, and treating with precipitated copper as directed by Gattermann, the solution is filtered by the aid of the pump, and the residue well washed with dilute ammonia; the ammoniacal washings are allowed to mix with the sulphuric acid filtrate. Concentrated ferric chloride solution is then added to the solution, which still contains excess of sulphuric acid, until no further precipitate falls; the ferric salt separates as a bright orange-yellow precipitate, which is collected, well washed with water, and dried with the aid of a little alcohol. As 10 grams of aniline give 16 grams of dry ferric benzenesulphinate, the yield is practically theoretical:

1·1145 gave 0·1855 Fe_2O_3. Fe = 11·56.

$C_{18}H_{21}O_6S_3Fe$ requires Fe = 11·68 per cent.

This salt was incidentally prepared by O. Piloty (*Ber.*, 1896, **29**, 1563), who describes it as a characteristic yellow precipitate which gradually dissolves in dilute acids.

On treating the ferric benzenesulphinate with a slight excess of aqueous ammonia, filtering from ferric hydroxide, and acidifying with concentrated hydrochloric acid in the cold, benzenesulphinic acid separates in colourless needles melting at 85°. On treating the ferric salt (18 grams) with 33 per cent. aqueous ammonia (25 c.c.), containing ammonium chloride (2·5 grams), and running in sodium hypochlorite solution, reaction occurs in the cold; after a slight excess of hypochlorite has been added, the mixture is kept for an hour, and the suspended ferric hydroxide dissolved by addition of hydrochloric acid. Benzenesulphonamide remains suspended in the acid solution, and gives the correct melting point after filtration, washing, and drying.

Ferric o-*Toluenesulphinate,* $(C_6H_4Me\cdot SO\cdot O)_3Fe$.

On treating *o*-toluidine (10 grams) in the manner above described, ferric *o*-toluenesulphinate (14·5 grams) is obtained as a reddish-yellow powder:

1·3185 gave 0·2025 Fe_2O_3. Fe = 10·74.

$C_{19}H_{23}O_6S_3Fe$ requires Fe = 10·94 per cent.

The ammoniacal solution prepared from the ferric salt, when acidified with hydrochloric acid, yields a mixture of the sulphinic acid with its anhydride. *o*-Toluenesulphonamide, melting at 155°, is formed on treating the ferric salt with ammonia and sodium hypochlorite under the conditions described above.

Ferric p-*Toluenesulphinate*, $(C_6H_4Me\cdot SO\cdot O)_3Fe$.

p-Toluidine (10 grams) yields ferric *p*-toluenesulphinate (12·5 grams) as an orange-yellow powder by the process described above:

1·2295 gave 0·1890 Fe_2O_3. Fe = 10·76.

$C_{19}H_{23}O_6S_3Fe$ requires Fe = 10·94 per cent.

On adding hydrochloric acid to the ammoniacal solution prepared from the ferric salt, a mixture of the sulphinic acid with its anhydride is precipitated; this yields the acid, melting at 86—87°, on recrystallisation from water.

Ferric α-Naphthalenesulphinate, $(C_{10}H_7\cdot SO\cdot O)_3Fe$.

α-Naphthylamine (6 grams) yields ferric *α*-naphthalenesulphinate (10 grams) as an orange-yellow precipitate on treatment in the specified manner:

1·3660 gave 0·1740 Fe_2O_3. Fe = 8·92.

$C_{30}H_{21}O_6S_3Fe$ requires Fe = 8·89 per cent.

On acidifying the ammoniacal solution obtained from the ferric salt, a mixture of the sulphinic acid and its anhydride separates, and on recrystallisation from water the acid is obtained in needles melting at 98—99°. The ferric salt is decomposed by sodium carbonate solution, and on adding sodium hypochlorite solution in slight excess to the filtrate, *α*-naphthalenesulphonyl chloride separates in the crystalline state and melts at 67°. On treating the ferric salt with ammonia and hypochlorite as previously described, *α*-naphthalenesulphonamide, melting at 152°, is obtained.

Ferric β-Naphthalenesulphinate, $(C_{10}H_7\cdot SO\cdot O)_3Fe$.

β-Naphthylamine (6 grams), when treated in a similar manner to its isomeride, gives ferric *β*-naphthalenesulphinate (10 grams) as a yellow powder:

1·1410 gave 0·1515 Fe_2O_3. Fe = 9·29.

$C_{30}H_{21}O_6S_3Fe$ requires Fe = 8·89 per cent.

The free sulphinic acid is separated from the ferric salt in the same way as before, and forms crystalline needles melting at 104—104·5°. The iron salt, treated with sodium carbonate and hypochlorite, gives *β*-naphthalenesulphonyl chloride, melting at 75—76°.

The examples quoted above serve to show that the formation of a ferric salt insoluble in acids is a general property of the sulphinic acids, and that, by taking advantage of this very unusual property, easy methods become available for the preparation of the sulphinic acids, sulphonyl chlorides, and sulphonamides from primary aromatic amino-compounds.

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XLIV.—*The Decomposition and Sublimation of Ammonium Nitrite.*

BY PRAFULLA CHANDRA RÂY.

THE decomposition of ammonium nitrite in its aqueous solution has been investigated by Arndt (*Zeitsch. physikal. Chem.*, 1901, **39**, 1), Veley (Trans., 1903, **83**, 736), and others. The main object which these chemists had in view was to study the rate of evolution of nitrogen, the conclusion arrived at being that the evolution of the gas is in conformity with the law of mass action for a unimolecular reaction. During the last two years and more, I have been at intervals occupied with the problem of a simple synthesis of hydrazine from ammonium nitrite according to the equation:

$$\begin{matrix} NH_4{\cdot}NO_2 \\ + \\ NH_4{\cdot}NO_2 \end{matrix} = \begin{matrix} NH_2 \\ | \\ NH_2 \end{matrix} + 2H_2O + 2NO,$$

but although this expectation has not yet been realised, some interesting results have been obtained, which appear to be worthy of record. It will be shown below that an aqueous solution of ammonium nitrite, when heated in a vacuum at temperatures varying from 37° to 70°, decomposes only partly according to the well-known equation: $NH_4{\cdot}NO_2 = N_2 + 2H_2O$, a considerable portion of the salt (sometimes the major portion) subliming into the upper and cooler parts of the tube.

The method of carrying on the investigation was as follows: A solution of ammonium nitrite was prepared by double decomposition between recrystallised silver nitrite and pure ammonium chloride, and sometimes between barium nitrite and ammonium sulphate. Care was taken that the solution of ammonium nitrite contained in every case a very slight excess of silver nitrite or of barium nitrite, so that on the addition of dilute hydrochloric or sulphuric acid respectively, a faint opalescence was noticed. This was to ensure the total absence of ammonium chloride or of ammonium sulphate in the solution of ammonium nitrite.

About 2 to 4 c.c. of the solution of the salt thus prepared were introduced into a glass tube of 1·3 cm. diameter and 63 cm. length. As the liquid bumps during the earlier stages of heating, the tube was provided with a trap to guard against the contingency of even a trace of the liquid being carried over into the Sprengel pump. The lower part of the tube was immersed in a beaker containing water, into which a thermometer was plunged. The details of a few typical experiments are given below.

Experiment I.—Two c.c. of a solution of ammonium nitrite were taken; an evaluation by the "urea" method gave for 1 c.c. of the solution 7·7 c.c. of nitrogen at 23° and 760 mm. (=a 2 per cent. solution). During the first stage of heating, the temperature was kept at 30° to 32°; only water distilled over, and when a certain degree of concentration had been attained, minute bubbles began to be given off. The temperature was gradually raised to 70°, to complete the decomposition. A distinct sublimate was, however, invariably noticed in the upper part of the tube. The sublimate was washed out and made up to a given bulk. An aliquot portion of it liberated iodine copiously from a solution of potassium iodide acidified with dilute sulphuric acid; another portion yielded nitrogen by the "urea" method, and nitric oxide by the Crum-Frankland method, the volumes of the gases being identical. The ammonia in the base was also estimated by nesslerisation, and it was found that the ratio of nitrogen in the base to that in the acid radicle was 1 : 1.

It was thus proved that the sublimate was a nitrite pure and simple. The gas collected in the Sprengel pump reservoir was tested with a solution of ferrous sulphate. A pale brown ring was obtained, but the amount absorbed was scarcely measurable.

The volume of the gas collected as above was 13·6 c.c., and that derived from the sublimate was 1·6 c.c.; total volume = 15·2 c.c. at 23° and 760 mm., the calculated volume of the gas at the same temperature and pressure being 15·4 c.c.: difference = 0·2 c.c.*

Experiment II.—Four c.c. of the solution, the same as used in experiment I, were taken, and the gases were also measured at the same temperature and pressure.

Volume of the gas from the Sprengel pump..............................	26·8 c.c.
,, ,, ,, sublimate by the "urea" method ...	3·2 ,,
Total volume	30·0 c.c.

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* It may be pointed out here that, although, by the "urea" method, only the radicle NO_2 is attacked, the amount of nitrogen set free is really doubled, and hence the volume of nitrogen as yielded by the decomposition of ammonium nitrite by heat is identical with that yielded by the "urea" method.

The calculated amount is 30·8 c.c. The deficiency, as will be shown below, is due to traces of the sublimate being drawn into the "Sprengel" tube.

Experiment III.—Liquid taken = 2 c.c. In the present experiment the other conditions were exactly the same as in the preceding ones, but the temperature of the bath was kept at 57—60°.

The gas collected in the Sprengel reservoir	9·7 c.c.
The gas from the sublimate by the "urea" method.........	3·6 ,,
Total volume...............	13·3 c.c.

The calculated amount of nitrogen in 2 c.c. of liquid = 15·4 c.c.: deficiency = 2·1 c.c. In fact, the lower the temperature at which the decomposition is effected the larger is the amount of the sublimate formed, and of the portion of it which finds its way into the "Sprengel" tube.

Experiment IV.—The ammonium nitrite solution used in this case was prepared by the interaction of barium nitrite and ammonium sulphate.

The volume of the nitrite solution was 4 c.c. (= 0·7 per cent. solution, approximately). The temperature of the bath was slowly raised to 35°, but as the distillation of the water was very slow at that temperature, it was gradually raised to 40—45°, and kept constant at 45°. It was noticed, as before, that when the solution had attained a definite degree of concentration, minute bubbles of nitrogen began to be given off; but as the rate of decomposition was very slow, the temperature was raised to 50°. After a time, when the water had almost evaporated, a thick, semi-solid magma was obtained, the salt separating out in fine needles and bubbles of gas being given off continuously. Owing to the fact that water is one of the products of its decomposition, the salt always remained moist. When, finally, the temperature of the bath was raised to 70°, most of the salt volatilised, a small portion only undergoing decomposition. The gas was collected in two separate instalments, the first being that given off during crystallisation and sublimation, and the second portion being that yielded by heating the sublimate itself. In order that the sublimate may be seen to advantage, it is necessary to heat the upper portion of the tube just enough to prevent moisture being deposited, which by dissolving ammonium nitrite would mask the real nature of the sublimate. The sublimate was sometimes deposited as a thin incrustation, and sometimes in the shape of fine flakes, and it could be moved up and down the tube by simply heating from outside with a naked flame. To effect as complete a decomposition of the sublimate as possible, the entire length of the tube was kept heated; but in spite of this precaution a small fraction of it invariably made its way into the "Sprengel" tube.

In the present experiment the first instalment of gas amounted to 1·9 c.c., and the second to 6·8 c.c.: total volume = 8·7 c.c. Four c.c. of a solution of ammonium nitrite gave by the "urea" process 10·8 c.c. of nitrogen at 23° and 760 mm. The deficiency is accounted for by the ammonium nitrite which entered into the "Sprengel." The first instalment of gas gave no coloration with a solution of ferrous sulphate; but the second portion, when similarly treated, gave a dark brown ring with a diminution in volume of 0·4 c.c., and when it was shaken up with water no further absorption took place, thus proving the presence of nitric oxide and the absence of nitrous oxide. The ratio of nitrogen to nitric oxide is thus equal to $\frac{6{\cdot}4}{0{\cdot}4} = 16$.

It is unnecessary to multiply instances of the decomposition of the salt, the nature of the decomposition products being sufficiently indicated by the above typical experiments. It remains to lay stress on the fact that the lower the temperature at which the solution is evaporated the larger is the yield of the crystallised salt.

It has been stated by several observers that the deliquescent crystals of this salt explode on heating to 60—70°, and that even acid solutions of it sometimes undergo similar decompositions (Berthelot, *Bull. Soc. chim.*, 1874, [ii], **21**, 55; Sörensen, *Zeitsch. anorg. Chem.*, 1894, **7**, 33). In one experiment the tube was detached from the "Sprengel," and the crystals at the bottom were heated directly with a burner. No explosion, however, took place.

The question naturally arises: Does ammonium nitrite volatilise *as such*, or is it simply a case of dissociation? If the latter hypothesis is accepted, it follows that nitrous acid can exist by itself at least for the time being. It has been shown, with regard to ammonium chloride, that under diminished pressure and in an atmosphere of ammonia it volatilises without dissociation (Neuberg, *Ber.*, 1891, **24**, 2543); and Baker has also proved that if ammonium chloride is free from every trace of moisture, it has the normal vapour density even under ordinary atmospheric pressure. Experiments have been undertaken to throw light on this point, but for the present the question must be left an open one. It should also be remembered in this connexion that Berthelot has shown that if ammonium nitrate is gently heated (the temperature being below 200°), it decomposes into water and nitrous oxide, but a portion of the salt at the same time sublimes unchanged (*Compt. rend.*, 1876, **82**, 932). He seems inclined to regard it as a case of sublimation without preliminary dissociation.

Summary.

From the foregoing investigation, it follows that when an aqueous solution of ammonium nitrite is heated in a vacuum at 37—40°, only a very small portion of the salt decomposes according to the equation: $NH_4\cdot NO_2 = 2H_2O + N_2$, most of the salt crystallising out. If the temperature is now gradually raised to 70°, slow decomposition goes on according to the above equation, but the major portion sublimes unchanged. When this sublimate is heated by means of a naked flame, the gaseous products are nitrogen and nitric oxide, the latter often amounting to as much as 6 per cent.

I avail myself of this opportunity to express my sincere thanks to Mr. Atul Chandra Ghosha, M.A., for the care and diligence with which he carried out some of the details of the experiments.

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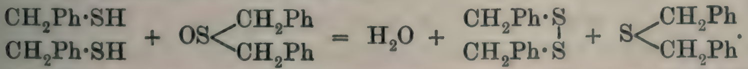
XLV.—*Benzyl Sulphoxide: a Possible Example of Dynamic Isomerism.*

By John Armstrong Smythe.

The ease with which mercaptans condense with ketones suggests that similar reactions may take place between the mercaptans and the structural analogues of the ketones, namely, the sulphoxides. The attempt to condense together benzyl mercaptan and benzyl sulphoxide led to the detailed investigation of the latter which forms the main subject-matter of this communication. In the preliminary experiments both benzyl sulphide and benzyl disulphide were identified among the products of reaction, so that it seemed at first that the mercaptan and sulphoxide had reacted, not, indeed, to furnish the expected mercaptal, but its proximate substituents, thus:



$$\begin{matrix}CH_2Ph\cdot SH\\CH_2Ph\cdot SH\end{matrix} + OS{<}\begin{matrix}CH_2Ph\\CH_2Ph\end{matrix} = H_2O + \begin{matrix}CH_2Ph\cdot S\\ | \\ CH_2Ph\cdot S\end{matrix} + S{<}\begin{matrix}CH_2Ph\\CH_2Ph\end{matrix}.$$

Further study of the reaction showed, however, that the disulphide was greatly in excess of the sulphide, whence it was apparent that if the above reaction had taken place, it had done so to a relatively small extent; and the control experiments proved that the condensing agent, hydrochloric acid, has a specific action on the mercaptan and the sulphoxide, which, in the latter case, results in the formation of benzyl disulphide and sulphide. The action of hydrochloric acid on benzyl mercaptan is still under investigation; its action on benzyl sulphoxide will now be considered in detail.

One of the most striking features of this reaction is the extreme ease with which it takes place. If dry hydrogen chloride, for instance, is led on to the surface of dry benzyl sulphoxide, immediate action sets in, heat being evolved, and the mass becoming pasty from the formation of benzaldehyde and benzyl chloride. When the sulphoxide is dissolved in a solvent, it suffices to saturate this at the ordinary temperature to complete the decomposition. For reasons which will become apparent later, this reaction has been studied under a variety of conditions and in many different solvents, and an attempt has been made to estimate the products quantitatively. The method of working adopted is as follows:

The Action of Hydrochloric Acid on Benzyl Sulphoxide.

1. *Method.*—A weighed quantity of pure benzyl sulphoxide (m. p. 133°) is dissolved, or partly so, in four to ten times its weight of solvent, and dry hydrogen chloride passed in until the liquid is completely saturated. The reaction is carried out sometimes at the ordinary temperature, at other times on the water-bath, a suitable condensing arrangement being used in the latter case, and the passing of the gas into the liquid being continued during the cooling stage. In the earlier experiments, special efforts were made to trap volatile compounds, such as sulphur chloride, which might possibly be formed in the reaction, but such were not detected, and the quantitative data prove that they are not formed in appreciable quantity.

As soon as saturation is reached, the reaction is complete. On distilling in a current of steam, excess of the solvent passes over first, and then an oil heavier than water; the residue is cooled and agitated to granulate the solid.

The *distillate* is extracted with ether (where acetic acid has been used it is advisable to neutralise this before extraction), the ethereal solution dried, and the ether evaporated. The residual oil, despite its constant boiling point (179°), is a mixture of benzyl chloride and benzaldehyde, sometimes containing a little mercaptan. The method used to separate these quantitatively is to shake the ethereal solution with a strong, freshly-prepared solution of sodium hydrogen sulphite. After keeping for several hours, with frequent shakings, the crystals of the hydrogen sulphite compound are collected, washed with ether, then dried on a porous plate, and weighed. Distillation of these with sodium carbonate in a current of steam yields the free aldehyde, which can be collected and weighed, when in sufficient quantity, as a check on the bisulphite determination. The ethereal liquors from the hydrogen sulphite compound are then dried and distilled from a tared flask, and the weight of the benzyl chloride is determined after all the ether has been expelled. The identity of the benzyl chloride is then fixed by a determination of its boiling point. When benzyl mercaptan is present, it can be estimated, after removal of the aldehyde and ether, by shaking the residual oil with standard iodine solution.

The *residue* from the original steam distillation is ground with water, filtered, and weighed when dry. It is then submitted to an exhaustive process of fractional crystallisation. It may contain two or three of the following compounds, namely, benzyl sulphide, benzyl disulphide, benzyl disulphoxide, and benzaldehyde-benzylmercaptal. The isolation of these compounds in a pure state presents no special difficulties, but the attempt to estimate them quantitatively proved very laborious, for they do not differ markedly in solubility in the various solvents used, and a certain amount of loss was inevitable in the manipulation of sometimes more than fifty crops of crystals and as many mother liquors, and in the melting-point determinations of these crops. By careful working, however, the loss may be reduced to a low figure, and, omitting three of the earlier experiments made when the necessary skill had not been acquired, the average loss of solid products in nine reactions was only about 9 per cent. Alcohol was the chief solvent used, generally alone, but sometimes in admixture with ether and chloroform. Ethyl acetate and glacial acetic acid rendered good service in some cases, and small quantities of cold ether were found especially valuable in the separation of the disulphide from the disulphoxide. Cooling by ice or a freezing mixture was also advantageous in the treatment of residual liquors, which sometimes tend to become oily, and are readily soluble in ether, but not in other solvents.

From the above description it will readily be understood that exact quantitative data of this reaction are not attainable; results of considerable value, however, for a correct understanding of the reaction can be obtained, and duplicate determinations agree fairly satisfactorily with a maximum deviation of, say, one constituent of about 3 per cent.

2. *Identification of the Products of Reaction.*—As most of the substances mentioned are well known, organic analysis was used but sparingly for the purposes of identification. It may be convenient to bring together now such analyses as were made, and also to summarise the chief properties of the compounds which, along with odour, crystalline habit, etc., served as a means of identification throughout the whole course of the work. In the case of the solid compounds,

the determination of melting points of samples mixed with standard preparations was often resorted to as a check.

Benzyl chloride, b. p. 179°, yields with alcoholic sodium sulphide an oil with an odour of benzyl mercaptan, benzyl sulphide (m. p. 49°), and sodium chloride; oxidised by potassium permanganate to benzoic acid.

Benzyl mercaptan, $C_6H_5{\cdot}CH_2{\cdot}SH$, b. p. 195°, decolorises iodine solution, being oxidised to benzyl disulphide (m. p. 71°).

Benzyl sulphide, $(C_6H_5{\cdot}CH_2)_2S$, m. p. 49°, is oxidised by nitric acid to benzyl sulphoxide, m. p. 133°. Of the following analyses, I and III are from samples prepared when acetic acid was the solvent; II, when chloroform was the solvent. (For analyses I, II, IV, V, VIII, I am greatly indebted to Mr. H. Blair, F.C.S.):

I. 0·1148 gave 0·3322 CO_2 and 0·0675 H_2O. C = 78·92; H = 6·53.
II. 0·1275 „ 0·3681 CO_2 „ 0·0794 H_2O. C = 78·71; H = 6·92.
III. 0·1764 „ 0·1913 $BaSO_4$. S = 14·86.
$C_{14}H_{14}S$ requires C = 78·50; H = 6·54; S = 14·95 per cent.

Benzyl disulphide, $(C_6H_5{\cdot}CH_2)_2S_2$, m. p. 71°. When a cold alcoholic solution of this compound is mixed with one of silver nitrate, crystals of a double compound appear in the liquid, and develop without motion in spherical form until the whole liquid becomes filled with solid matter.

Analyses:—IV and VI from samples prepared in acetic acid solution; V, in alcoholic solution:

IV. 0·1313 gave 0·3280 CO_2 and 0·0674 H_2O. C = 68·13; H = 5·70.
V. 0·3610 „ 0·9021 CO_2 „ 0·1861 H_2O. C = 68·14; H = 5·73.
VI. 0·2340 „ 0·4460 $BaSO_4$. S = 26·18.
$C_{14}H_{14}S_2$ requires C = 68·30; H = 5·69; S = 26·07 per cent.

Benzaldehyde-benzylmercaptal, $C_6H_5{\cdot}CH(S{\cdot}CH_2{\cdot}C_6H_5)_2$, m. p. 61°. Many specimens of this compound, prepared in different ways to be described later, as well as by the direct condensation of benzyl mercaptan and benzaldehyde, have never given the melting point, 64°, stated by Fromm and Junius (*Ber.*, 1895, **28**, 1111). The compound is partly hydrolysed by hydrochloric acid, yielding thereby benzaldehyde and benzyl mercaptan.

Benzyl disuphoxide, $(C_6H_5{\cdot}CH_2)_2O_2S_2$, m. p. 109°. Analyses:—VII and IX from samples prepared in acetic acid solution; VIII, in alcoholic solution:

VII. 0·1626 gave 0·3612 CO_2 and 0·0732 H_2O. C = 60·57; H = 5·00.
VIII. 0·1101 „ 0·2431 CO_2 „ 0·0499 H_2O. C = 60·21; H = 5·04.
XI. 0·1307 „ 0·2210 $BaSO_4$. S = 23·20.
$C_{14}H_{14}O_2S_2$ requires C = 60·44; H = 5·04; S = 23·03 per cent.

Since these analyses were made, this compound has been described by Fromm and Palma (*Ber.*, 1906, **39**, 3308), and more recently by Hinsberg (*Ber.*, 1908, **41**, 2836) and others, and their description agrees with my own observations.

3. *The Quantitative Results.*—The complete quantitative data will now be given. In all cases, except when otherwise stated, the reaction was carried out at the ordinary temperature, and the stream of hydrogen chloride was regulated so that no considerable heating took place.

Reaction between Benzyl Sulphoxide and Hydrochloric Acid.
Experimental Results.

				Pure products (grams).					
Solvent.	Sulphoxide taken (grams).	Crude solid products (grams).	$Ph{\cdot}CHO$.	$Ph{\cdot}CH_2Cl$.	$Ph{\cdot}CH_2{\cdot}SH$.	$(CH_2Ph)_2S_2$.	$(CH_2Ph)_2S$.	$(CH_2Ph)_2O_2S_2$.	$CHPh(S{\cdot}CH_2Ph)_2$.
Alcohol (85 per cent.)..	20	12·1	0·4	7·1	—	2·70	2·90	5·50	—
Acetic acid (75 per cent.)	40	14·6	0·25	11·2	—	3·56	2·16	7·62	—
Glacial acetic acid	50	27·4	6·9	16·7	—	18·70	0·60	2·70	—
Glacial acetic acid + acetic anhydride	20	11·1	3·9	5·0	trace	8·75	0·10	—	1·09
No solvent	20	11·73	3·05	6·2	—	6·72	1·73	2·27	—
Water (hot)	15	10·0	3·1	1·5	trace	3·60	2·75	0·90	—
Ether (wet)	20	12·7	3·7	3·6	trace	6·27	3·86	1·32	—
Ether (dry)	20	12·6	5·7	2·0	trace	7·31	4·18	—	—
Chloroform (cold)	25	15·8	6·9	1·8	—	8·95	5·95	0·08	—
Chloroform (hot).........	20	12·7	5·8	1·2	—	6·65	5·57	—	—
Benzene	25	15·0	5·9	1·2	—	7·50	5·60	—	—
Carbon tetrachloride (hot)	25	16·0	7·3	0·3	0·3	6·35	4·75	—	0·55

In expressing these results in percentage values, the error due to unavoidable loss in the fractionation of the solid products is minimised by distributing this loss in proportion to the weights of the pure solid compounds obtained. For example, in the reaction in dry ethereal solution the solid product weighed 12·6 grams, and this on fractionation yielded 7·31 grams of benzyl disulphide and 4·18 grams of benzyl sulphide; the loss is thus 1·11 grams, and this amount, distributed proportionally to the weights of pure disulphide and sulphide obtained, raises the weights of these to 8·02 and 4·58 grams respectively.

The percentage yields in the various reactions, calculated from the above data and corrected for loss on fractionation of the solid products as just described, are given in the next table. In the last column are grouped together benzaldehyde-benzylmercaptal, benzyl mercaptan, and the equivalent in benzaldehyde of these two, since the amounts given of the three compounds are all furnished in one reaction.

Reaction between Benzyl Sulphoxide and Hydrochloric Acid. Percentage Yields of Organic Products.

Solvent.	$Ph{\cdot}CHO$.	$Ph{\cdot}CH_2Cl$.	$(CH_2Ph)_2S_2$.	$(CH_2Ph)_2S$.	$(CH_2Ph)_2S_2O_2$.	$CH_2Ph{\cdot}SH$, $Ph{\cdot}CHO$, and $CHPh(S{\cdot}CH_2Ph)_2$.
Dilute alcohol.........	2·04	36·23	14·80	16·32	30·62	—
Dilute acetic acid	0·96	43·00	14·93	9·09	32·32	—
Glacial acetic acid	13·50	32·80	45·70	1·50	6·50	—
Glacial acetic acid + acetic anhydride......	17·55	25·00	48·85	0·55	—	8·05
No solvent	14·54	29·56	35·05	9·02	11·83	—
Water (hot)........... ...	21·22	10·28	33·95	26·05	8·50	—
Ether (wet)	18·50	18·00	34·75	21·40	7·35	—
Ether (dry)	28·08	9·85	39·50	22·57	—	—
Chloroform (cold)	28·16	7·35	38·52	25·60	0·37	—
Chloroform (hot).........	29·44	6·09	35·07	29·40	—	—
Benzene	26·70	5·40	38·90	29·00	—	—
Carbon tetrachloride (hot)	29·92	1·25	36·48	27·28	—	5·07

4. *Explanation of the Reaction: the Hypothesis of Tautomerism.*—On the basis of the ordinarily-accepted constitutional formula for benzyl sulphoxide, namely, $CH_2Ph{\cdot}SO{\cdot}CH_2Ph$, it is not difficult to understand the formation of many of the products derived from it by reaction with hydrochloric acid. The benzyl sulphide, for example, may be regarded as a simple reduction product of the sulphoxide, and the chlorine set free in this operation could produce the disulphide and disulphoxide* by withdrawing the benzyl radicle from the sulphide or a further quantity of the sulphoxide. It is much less easy to understand the formation of benzaldehyde and benzyl mercaptan (and their condensation product, benzaldehyde-benzylmercaptal), the first of which is produced very readily in the reaction under all conditions. To account for the benzaldehyde it would be necessary to assume, first, the disruption of the sulphoxide molecule and then the combination of sulphoxidic oxygen with carbon, and

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* The experiments of Fromm and Palma (*Ber.*, 1906, **39**, 3308) and Hinsberg (*Ber.*, 1908, **41**, 2836), who have lately attacked the problem of the constitution of the disulphoxides, are by no means convincing, although, on the whole, they probably favour the constitution accepted in this paper, namely,

$$CH_2Ph{\cdot}SO{\cdot}SO{\cdot}CH_2Ph.$$

the explanation of the formation of the mercaptan would involve the assumption of, perhaps, even less probable molecular changes.

If we assume, however, that benzyl sulphoxide may exist in the form of hydroxybenzyl sulphide, $OH\cdot CHPh\cdot S\cdot CH_2Ph$, then much of the difficulty vanishes, for a compound of this constitution might be expected to yield quite readily both benzaldehyde and benzyl mercaptan; at any rate, the formation of these two compounds from a substance of such constitution would impose no strain on the imagination. In addition, the simultaneous formation of benzaldehyde, benzyl disulphide, and benzyl sulphide would be easily accounted for.

There are thus at least two possible constitutional formulæ for benzyl sulphoxide, each of which has certain merits, in that it gives the best account of some of the products of its reaction with hydrochloric acid. Now a glance at the table of results (p. 353) reveals the fact that in seven reactions, compounds are simultaneously produced, the ready explanation of which requires the co-existence of both forms of the sulphoxide. One is thus led to the view that the sulphoxide in solution, under certain conditions, may exist in two forms, in one of which the oxygen is united with sulphur, and in the other with carbon. Further development of the subject indicates that these forms are mutually convertible, and a solution of the compound under certain conditions may be regarded as containing the dynamic isomerides in equilibrium, thus:

$$CH_2Ph\cdot SO\cdot CH_2Ph \rightleftharpoons HO\cdot CHPh\cdot S\cdot CH_2Ph.$$

These forms may be called, by analogy, the ketonic and the enolic. The factors on which the equilibrium depends and the mechanism of conversion will be considered later.

On the assumption of the existence of these tautomeric forms, it is now possible to develop a series of equations expressing the reactions between one or other forms, or mixtures of both, and hydrochloric acid, which give a complete and easy account of the products formed and are verifiable by the quantitative data.

The Equations of Reaction.

A. $4CH_2Ph\cdot SO\cdot CH_2Ph + 4HCl =$
$CH_2Ph\cdot SO\cdot SO\cdot CH_2Ph + 4CH_2PhCl + CH_2Ph\cdot S_2\cdot CH_2Ph + 2H_2O.$

B. $3CH_2Ph\cdot SO\cdot CH_2Ph + 2HCl =$
$CH_2Ph\cdot SO\cdot SO\cdot CH_2Ph + 2CH_2PhCl + CH_2Ph\cdot S\cdot CH_2Ph + H_2O.$

C. $CH_2Ph\cdot SO\cdot CH_2Ph + CH_2Ph\cdot S\cdot CHPh\cdot OH + 2HCl =$
$CH_2Ph\cdot S_2\cdot CH_2Ph + CH_2PhCl + Ph\cdot CHO + H_2O + HCl.$

D. $2CH_2Ph\cdot S\cdot CHPh\cdot OH + CH_2Ph\cdot SO\cdot CH_2Ph + 2HCl =$
$CH_2Ph\cdot S_2\cdot CH_2Ph + 2Ph\cdot CHO + CH_2Ph\cdot S\cdot CH_2Ph + H_2O + 2HCl.$

E. $CH_2Ph\cdot S\cdot CHPh\cdot OH + HCl = Ph\cdot CHO + CH_2Ph\cdot SH + HCl.$

It will be noticed in these equations that the essential reaction is the reduction of the sulphoxide by hydrochloric acid, the chlorine made available for reaction by this process being employed either in oxidation of the group $CHPh{\cdot}OH$ to benzaldehyde, or in combining with the benzyl radicle to form benzyl chloride. In equations *D* and *E* the hydrochloric acid is completely regenerated, so that these reactions may take place without its direct intervention (its function being that of a condensing agent). In fact, equation *D* may be regarded as expressing a kind of condensation reaction between the enolic and ketonic forms of the sulphoxide, thus:

$$2CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH + CH_2Ph{\cdot}SO{\cdot}CH_2Ph = CH_2Ph{\cdot}S_2{\cdot}CH_2Ph + 2Ph{\cdot}CHO + CH_2Ph{\cdot}S{\cdot}CH_2Ph + H_2O;$$

and *E*, as virtually a reaction of simple decomposition induced by the instability of the enolic form:

$$CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH = Ph{\cdot}CHO + CH_2Ph{\cdot}SH.$$

The latter view finds support in the reactions (to be described later) which the sulphoxide undergoes with sulphuric acid and with dehydrating agents.

It may be mentioned here that other equations have not been suggested by a careful study of the question, and that, although reaction always takes place according to more than one equation, the amount of sulphoxide decomposed according to any single equation may reach from 60 to 90 per cent. by selection of suitable conditions, and the decomposition of the enolic form into aldehyde and mercaptan by dehydrating agents is probably quantitative.

The only certain secondary reaction which takes place is that between the products from reaction *E*, which condense to form benzaldehyde-benzylmercaptal:

$$Ph{\cdot}CHO + 2HS{\cdot}CH_2Ph = CHPh(S{\cdot}CH_2Ph)_2 + H_2O.$$

The chlorine set free by the oxidation of the hydrochloric acid by the sulphoxide might be thought to enter into other reactions than the two described above, and, on first consideration, might be held responsible for the tautomeric change by substitution in the sulphide, as illustrated in the following equations:

$$CH_2Ph{\cdot}SO{\cdot}CH_2Ph + 2HCl = CH_2Ph{\cdot}S{\cdot}CH_2Ph + H_2O + Cl_2.$$
$$CH_2Ph{\cdot}S{\cdot}CH_2Ph + Cl_2 = CH_2Ph{\cdot}S{\cdot}CHClPh + HCl.$$
$$CH_2Ph{\cdot}S{\cdot}CHClPh + H_2O = CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH + HCl.$$

The net result of these reactions is the simple conversion of the ketonic form of the sulphoxide into the enolic. Such a process, whilst not affecting the question of the derivation of the equations, is possible, although its assumption is by no means necessary, as it will be shown later that a practically quantitative conversion of ketonic into enolic form can be brought about by acetic anhydride, in which case there is no chance of reduction of the sulphoxide, little or no opportunity for substitution, and no water present.

The only other likely reaction for the chlorine to enter into is with benzyl mercaptan, which it might oxidise to benzyl disulphide. This reaction would take place in the following stages:

$$CH_2Ph{\cdot}SO{\cdot}CH_2Ph + 2HCl = CH_2Ph{\cdot}S{\cdot}CH_2Ph + H_2O + Cl_2;$$
$$2CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH = 2Ph{\cdot}CHO + 2CH_2Ph{\cdot}SH;$$
$$2CH_2Ph{\cdot}SH + Cl_2 = (CH_2Ph)_2S_2 + 2HCl.$$

Adding these equations together, we get:

$$CH_2Ph{\cdot}SO{\cdot}CH_2Ph + 2CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH = (CH_2Ph)_2S_2 + 2Ph{\cdot}CHO + (CH_2Ph)_2S,$$

and this is identical with equation *D*, so that any such reaction of the chlorine may be neglected.

The quantitative data may now be used for testing the hypothesis of tautomerism which has been brought forward, and which finds its expression in the five equations of reaction. The reaction in each solvent takes place in accordance with more than one equation; there are thus several "constituent reactions" (as they may be called) which make up the complete reaction, each of which is represented by one of the equations of reaction. Some compounds are only formed in one of the constituent reactions, so that the extent to which this has proceeded is determinable; if the complete reaction embraces another constituent reaction, the extent to which this has taken place is found by difference.

An example may be quoted to make the method of procedure clear. In dry ethereal solution the products of reaction and the percentage quantities of these are:

Benzaldehyde	28·08
Benzyl chloride	9·85
,, disulphide	39·50
,, sulphide	22·57
	100·00

No disulphoxide or mercaptan (or benzaldehyde-benzylmercaptal) is formed, so that reactions *A*, *B*, and *E* are ruled out. The benzyl chloride can only come from *C*, the sulphide only from *D*, and the other products from *C* and *D*. The percentage amounts of organic products from these two reactions are:

	C.	*D.*
Benzaldehyde	22·2	31·5
Benzyl chloride	26·4	—
,, disulphide	51·4	36·6
,, sulphide	—	31·9

To furnish 9·85 grams of benzyl chloride, 37·3 grams of organic products would have to be generated in reaction *C*, and the remaining

62·7 grams must thus have been produced in reaction *D*. The products would then be :

	From 37·3 grams decomposed in reaction *C*.	From 62·7 grams decomposed in reaction *D*.	Sum (calculated).	Found.
Benzaldehyde	8·28	19·75	28·03	28·08
Benzyl chloride	9·85	—	9·85	9·85
,, disulphide ...	19·18	22·95	42·13	39·50
,, sulphide......	—	20·00	20·00	22·57
			100·01	100·00

and the total amount of products calculated in this way agrees satisfactorily with the experimental data.

To ascertain what amounts of benzyl sulphoxide have reacted to yield these quantities of the various products, it must be remembered that in reaction *C*, 100 grams of sulphoxide generate 104 grams of organic products, and in reaction *D*, the same amount of sulphoxide yields 97·4 grams of organic products. Consequently, 37·3 grams of products in reaction *C* arise from 35·9 grams of sulphoxide, and 62·7 grams of products in *D* from 64·4 grams of sulphoxide. Thus it follows that in the reaction between hydrochloric acid and benzyl sulphoxide in ethereal solution, 35·8 per cent. of the sulphoxide is decomposed according to equation *C*, and 64·2 per cent. according to equation *D*.

The following table gives the comparison of the experimental results with the calculations made in the manner just described. The substantial agreement of all the quantities calculated with those actually determined may be held to verify the equations, and consequently to justify the hypothesis on which they are founded.

Comparison of Experimental with Calculated Results.

		Percentage amount of organic products generated in each reaction.					
Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	$Ph\cdot CHO$.	CH_2PhCl.	$(CH_2Ph)_2S_2$.	$(CH_2Ph)_2S$.	$(CH_2Ph)_2S_2O_2$.	$CHPh(S\cdot CH_2Ph)_2$, $CH_2Ph\cdot SH$, and $Ph\cdot CHO$.
Dilute ethyl alcohol.	29·1 *A*	—	14·73	7·14	—	8·07	—
	60·5 *B*	—	20·35	—	17·22	22·44	—
	10·4 *C*	2·22	2·64	5·14	—	—	—
Calculated ...		2·22	37·72	12·28	17·22	30·51	—
Found.........		2·04	36·23	14·80	16·32	30·61	—

Comparison of Experimental with Calculated Results (continued).

Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	Percentage amount of organic products generated in each reaction.					
		Ph·CHO.	CH_2PhCl.	$(CH_2Ph)_2S_2$.	$(CH_2Ph)_2S$.	$(CH_2Ph)_2S_2O_2$.	$CHPh(S·CH_2Ph)_2$, $CH_2Ph·SH$, and Ph·CHO.
Dilute acetic acid.	63·0 *A*	—	31·40	15·30	—	17·30	—
	32·4 *B*	—	10·80	—	9·10	11·90	—
	4·6 *C*	0·95	1·14	2·21	—	—	—
	Calculated ...	0·95	43·34	17·51	9·10	29·20	—
	Found.........	0·96	43·00	14·93	9·09	32·02	—
Glacial acetic acid.	33·4 *A*	—	17·20	8·36	—	9·44	—
	4·9 *B*	—	1·69	—	1·43	1·89	—
	61·7 *C*	13·32	15·84	30·84	—	—	—
	Calculated ...	13·32	34·73	39·20	1·43	11·33	—
	Found.........	13·50	32·80	45·70	1·50	6·50	—
Glacial acetic acid + acetic anhydride.	89·8 *C*	20·01	23·78	46·31	—	—	—
	1·6 *D*	0·47	—	0·55	0·48	—	—
	8·6 *E*	—	—	—	—	—	8·10
	Calculated ...	20·48	23·78	46·86	0·48	—	8·10
	Found.........	17·55	25·00	48·85	0·55	—	8·05
No solvent.	31·2 *B*	—	10·85	—	9·18	11·96	—
	68·8 *C*	15·10	17·95	34·96	—	—	—
	Calculated ...	15·10	28·80	34·96	9·18	11·96	—
	Found.........	14·54	29·56	35·05	9·08	11·80	—
Water (hot).	21·4 *B*	—	7·79	—	6·60	8·60	—
	9·6 *C*	2·22	2·64	5·14	—	—	—
	69·0 *D*	21·11	—	24·52	21·37	—	—
	Calculated ...	23·33	10·43	29·66	27·97	8·60	—
	Found.........	21·22	10·28	33·95	26·05	8·50	—
Ether (moist).	18·9 *B*	—	6·78	—	5·74	7·48	—
	39·2 *C*	8·88	10·56	20·56	—	—	—
	41·9 *D*	12·60	—	14·64	12·76	—	—
	Calculated ...	21·48	17·34	35·20	18·50	7·48	—
	Found.........	18·50	18·00	34·75	21·40	7·35	—
Ether (dry).	35·8 *C*	8·28	9·85	19·18	—	—	—
	64·2 *D*	17·95	—	22·95	20·00	—	—
	Calculated ...	28·03	9·85	42·13	20·00	—	—
	Found.........	28·08	9·85	39·50	22·57	—	—
Chloroform (cold).	0·9 *B*	—	0·34	—	0·29	0·37	—
	25·3 *C*	5·88	6·99	13·62	—	—	—
	73·8 *D*	22·84	—	26·53	23·13	—	—
	Calculated ...	28·72	7·33	40·15	23·42	0·37	—
	Found.........	28·16	7·35	38·52	25·60	0·37	—

Comparison of Experimental with Calculated Results (continued).

Solvent.	Percentage amount of sulphoxide decomposed in each reaction.	Percentage amount of organic products generated in each reaction.					
		Ph·CHO.	CH_2PhCl.	$(CH_2Ph)_2S_2$.	$(CH_2Ph)_2S$.	$(CH_2Ph)_2S_2O_2$.	$CHPh(S·CH_2Ph)_2$, $CH_2Ph·SH$, and Ph·CHO.
Chloroform (hot).	14·2 *C*	3·33	3·96	7·71	—	—	—
	85·8 *D*	26·77	—	31·11	27·11	—	—
	Calculated ...	30·10	3·96	38·82	27·11	—	—
	Found.........	29·44	6·09	35·07	29·40	—	—
Benzene.	19·0 *C*	4·44	5·28	10·25	—	—	—
	81·0 *D*	25·20	—	29·28	25·52	—	—
	Calculated ...	29·64	5·28	39·56	25·52	—	—
	Found.........	26·70	5·40	38·90	29·00	—	—
Carbon tetrachloride (hot).	9·4 *C*	2·22	2·64	5·14	—	—	—
	85·7 *D*	26·77	—	31·11	27·11	—	—
	4·9 *E*	—	—	—	—	—	5·00
	Calculated ...	28·99	2·64	36·25	27·11	—	5·00
	Found.........	29·92	1·25	36·48	27·28	—	5·07

A simple calculation from these results enables us now to accomplish a three-fold object; firstly, to attain a complete knowledge of the reaction in each solvent by determining the relative numbers of ketonic and enolic molecules which take part in each constituent reaction; secondly, to ascertain the composition at equilibrium under the particular conditions specified in each reaction; and thirdly, to bring the results into the form best suited for discussion. The method of calculation may be made clear by an example: In the five equations of reaction it will be observed that the ratio of the number of ketonic to enolic molecules is different in each case. Thus in *A* and *B* only ketonic molecules come into reaction, and in *E* only enolic molecules. The ratio of ketonic to enolic molecules in *C* is 1 : 1, and in *D* 1 : 2. Now, in the case of the reaction in moist ether, 19 per cent. roughly of the sulphoxide is transformed according to equation *B*, 39 per cent. according to equation *C*, and 42 per cent. according to equation *D*. Of 100 molecules of sulphoxide, 19 taking part in reaction *B* have thus been ketonic molecules, 19·5 each of ketonic and enolic molecules have taken part in reaction *C*, and $\frac{1}{3}$ of 42 ($=14$) ketonic and $\frac{2}{3}$ of 42 ($=28$) enolic molecules have reacted according to equation *D*. Tabulating these results we have:

	B.	*C.*	*D.*	Sum.
Percentage number of molecules of sulphoxide reacting according to equations *B*, *C*, and *D*..	19	39	42	100
Number of ketonic molecules entering into each constituent reaction	19	19·5	14	52·5 ketonic
Number of enolic molecules entering into each constituent reaction	—	19·5	28	47·5 enolic

The percentage composition at equilibrium under the conditions obtaining in this experiment has thus been:

$$\underset{52\cdot5}{\mathrm{CH_2Ph{\cdot}SO{\cdot}CH_2Ph}} \rightleftharpoons \underset{47\cdot5}{\mathrm{CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH}};$$

or, since, as will be shown later, the equilibrium has changed somewhat during the course of the reaction, these figures will represent the mean composition of the solution during the reaction.

Similar calculations for all the quantitative reactions are given in the following table:

		Percentage number of sulphoxide molecules entering into each constituent reaction.					
Solvent.		*A.*	*B.*	*C.*	*D.*	*E.*	Sum = (percentage composition at equilibrium).
Dilute acetic acid.	Total	63·0	32·4	4·6	—	—	
	Keto.	63·0	32·4	2·3	—	—	97·7 keto.
	Enol.	—	—	2·3	—	—	2·3 enol.
Dilute ethyl alcohol.	Total	29·1	60·5	10·4	—	—	
	Keto.	29·1	60·5	5·2	—	—	94·8 keto.
	Enol.	—	—	5·2	—	—	5·2 enol.
Glacial acetic acid.	Total	33·4	4·9	61·7	—	—	
	Keto.	33·4	4·9	30·8	—	—	69·1 keto.
	Enol.	—	—	30·9	—	—	30·9 enol.
No solvent.	Total	—	31·2	68·8	—	—	
	Keto.	—	31·2	34·4	—	—	65·6 keto.
	Enol.	—	—	34·4	—	—	34·4 enol.
Ether (moist).........	Total	—	18·9	39·2	41·9	—	
	Keto.	—	18·9	19·6	13·9	—	52·4 keto.
	Enol.	—	—	19·6	28·0	—	47·6 enol.
Water (hot)	Total	—	21·4	9·6	69·0	—	
	Keto.	—	21·4	4·8	23·0	—	49·2 keto.
	Enol.	—	—	4·8	46·0	—	50·8 enol.
Glacial acetic acid + acetic anhydride..	Total	—	—	89·8	1·6	8·6	
	Keto.	—	—	44·9	0·5	—	45·4 keto.
	Enol.	—	—	44·9	1·1	8·6	54·6 enol.
Ether (dry)............	Total	—	—	35·8	64·2	—	
	Keto.	—	—	17·9	21·4	—	39·3 keto.
	Enol.	—	—	17·9	42·8	—	60·7 enol.
Chloroform (cold) ...	Total	—	0·9	25·3	73·8	—	
	Keto.	—	0·9	12·6	24·6	—	38·1 keto.
	Enol.	—	—	12·7	49·2	—	67·9 enol.
Benzene	Total	—	—	19·0	81·0	—	
	Keto.	—	—	9·5	27·0	—	36·5 keto.
	Enol.	—	—	9·5	54·0	—	63·5 enol.
Chloroform (hot) ...	Total	—	—	14·2	85·8	—	
	Keto.	—	—	7·1	28·6	—	35·7 keto.
	Enol.	—	—	7·1	57·2	—	64·3 enol.
Carbon tetrachloride (hot)	Total	—	—	9·4	85·7	4·9	
	Keto.	—	—	4·7	28·6	—	33·3 keto.
	Enol.	—	—	4·7	57·1	4·9	66·7 enol.

Discussion of Results.

The expression of the quantitative results in the manner adopted in the above table brings out clearly some interesting facts connected with the reaction between hydrochloric acid and benzyl sulphoxide. It may be noted in the first place that, notwithstanding great diversities in experimental conditions, some sulphoxide has always been decomposed according to reaction *C*, into which a molecule each of the ketonic and enolic forms enters. Secondly, reaction *D* is favoured by the anhydrous solvents and by a high temperature. This may possibly be conditioned by the instability of the enolic form, the two forms reacting with each other, preferably to hydrochloric acid.

The solvents are clearly marked off into two classes, the aqueous and the anhydrous. In the former, the oxygen of the sulphoxide passes over chiefly to the disulphoxide, and in the latter, to benzaldehyde; or, looked at from another point of view, the aqueous solvents are characterised by containing a relatively high percentage of ketonic molecules at equilibrium, and the anhydrous solvents by a correspondingly large amount of enolic molecules. That the equilibrium between the two forms is brought about by a catalytic agent is a priori likely, and the facts seem to warrant the conclusion that water is the catalyst, and that the composition at equilibrium is a function of the concentration of water in the solvent.

Unfortunately, the available data concerning the solubility of water in organic liquids are of little use in this case for determining its influence exactly, because of the variation in solubility induced by the presence of hydrochloric acid and the products of its action on the sulphoxide. The general influence, however, is indisputable, and has been the subject of special study.

That the concentration of water is very low in the case of chloroform, benzene, and carbon tetrachloride, in which the percentage of enolic molecules is highest, is proved by its separating out in drops from the originally clear solution after the reaction is over. In the case of carbon tetrachloride, 150 c.c. of the dry solvent were used; the amount of water formed in the reaction from 25 grams of sulphoxide was about 0·6 gram, and judging from the appearance of the solvent after reaction, most of this water must have separated, so that its concentration would be very slight and speedily established. In dilute acetic acid and dilute alcohol, the quantity of water present from the beginning was so great that it is unlikely that the further amount formed in the reaction could have any effect on the equilibrium.

The three reactions in acetic acid show the influence of water-concentration on equilibrium very clearly. The glacial acid used had been purified by frequent liquations from the partly frozen acid, and the relative quantities of the materials brought together were:

	Sulphoxide.	Glacial acid.	Water.	Acetic anhydride.
Dilute acetic acid	1	2·5	1	—
Glacial acetic acetic	1	4·0	—	—
Glacial acetic acid + acetic anhydride	1	2·5	—	1

By reference to the figures showing the composition at equilibrium, it will be seen that the mixture of glacial acetic acid and acetic anhydride approximates in behaviour to the anhydrous solvents, which is unquestionably due to the removal of the water formed during reaction by the acetic anhydride, so that the water-concentration is kept low during the whole of the reaction. The glacial acetic acid partakes of the characters of both classes of solvents, from which it is evident that at first it acted as an anhydrous solvent, but with the progress of reaction it gradually changed its character by dissolving the water formed in the process, so that eventually it behaved more like an aqueous solvent. One may thus picture the equilibrium between the ketonic and enolic forms of the sulphoxide in glacial acetic acid as constantly changing during the reaction with hydrochloric acid, owing to the progressive conversion of enolic into ketonic molecules by the water produced in the reaction. The composition at equilibrium deduced from the data of reaction is thus a mean value.

The experiments in dry and moist ether are of particular interest in so far as they enable us to arrive at a rough quantitative estimate of the influence of water-concentration on equilibrium. In each case 20 grams of sulphoxide and 70 c.c. of ether were employed, and the reaction was carried out under similar conditions of temperature and velocity. The same sample of ether (free from alcohol) was used, the only difference being that in one experiment it was saturated with water, and in the other dried with calcium chloride and kept dry during the operation by being mixed with 4 grams of ground calcium chloride.

It is unlikely that calcium chloride, when in competition with dry hydrogen chloride for water, is so powerful a drying agent as under ordinary conditions, but it is safe to assume that the concentration of water in the "dry" ether was fairly small. The concentration in the moist ether can be calculated, knowing the solubility of water in ether and the amount of water formed in the reaction; these two quantities in the present case are 1·4 grams and 0·6 gram respectively, giving a mean value for the whole reaction of 1·7 grams or 2·4 per cent.

The ratio of the number of ketonic to enolic molecules at equilibrium in the two cases is 52·4 : 47·6 = 1 : 0·91 for the moist reaction, and 39·6 : 60·5 = 1 : 1·55 for the dry reaction. Thus, it follows that by diminishing the concentration of water in ether from 2·4 per cent. to a very low figure, the ratio of the number of enolic to ketonic molecules of the sulphoxide is increased in the ratio of 1 : 1·7.

The influence of temperature on the equilibrium of the two forms of benzyl sulphoxide, although not so closely studied as that of water-concentration, is yet clearly shown from the comparative experiments in hot and cold chloroform. From these it is obvious that increase in temperature brings about the conversion of some ketonic into enolic molecules; although having regard to the low boiling point of chloroform (61° for the pure compound; a little higher in the experiment owing to the presence of soluble substances), the effect is naturally small. It seems likely that the position of carbon tetrachloride in the list of solvents is partly due to the fact that the reaction in it was carried out at the boiling point (the sulphoxide is scarcely soluble in the solvent at the ordinary temperature). The reactions between hydrochloric acid and benzyl sulphoxide in the absence of solvent and in presence of water (that is, concentrated aqueous acid) are difficult to interpret, owing to the sulphoxide being largely attacked in each case when in the solid condition; but it seems probable that the increase of enolic molecules in the latter reaction is ascribable to the higher temperature, lessened perhaps to some extent by the influence of water on the small amount of sulphoxide dissolved.

On the question of the specific action of solvents on the equilibrium, little can be said, although there are not wanting indications that such action exists. The expectation that the mixture of acetic acid and its anhydride would have a more powerful enolising effect than the anhydrous solvents was not fulfilled, and the cause for that would appear to be inherent in the solvent. The close correspondence between enolising power and the electrolytic dissociating power of the solvents, as measured by their specific inductive capacities, points to a possible connexion between the two, and suggests that the slight apparent enolisation of the sulphoxide in the dissociating liquids may be due to the immunity from attack by hydrochloric acid conferred on the enolic form by its electrolytic dissociation. In the present state of our knowledge of the subject, however, it would perhaps be inadvisable to pursue this hypothesis further. The influence of dilution on equilibrium, which would probably throw some light on this subject, has not been studied.

The study of the reaction between hydrochloric acid and benzyl sulphoxide has thus led to the conclusion that the sulphoxide exists in two tautomeric forms, the ketonic and the enolic, and that the equilibrium between these is dependent chiefly on the concentration of water in the solution of the compound, also on the temperature, and possibly too on the nature of the solvent. The justification of this hypothesis rests chiefly on the quantitative data, although other facts, to be detailed shortly, confirm the general view adopted. Before passing on to these, however, it may be well to mention that this case of tautomerism is peculiar, in that it involves the transference of oxygen in the molecule, and, so far as I am aware, no such case has yet been described. Considering, however, the important part which water exerts on the equilibrium of the tautomerides, this fact presents no insuperable difficulty, for the conversion of one form into the other can be conceived as the result of a succession of intermolecular reactions involving the addition and loss of water, each corresponding stage differing from its predecessor only in the mode of union or elimination of the constituents of the water. The mechanism of tautomeric change can thus be represented by a series of more or less probable reversible reactions, somewhat as follows:

$$\begin{gathered}OH{\cdot}CHPh{\cdot}S{\cdot}CH_2Ph + H_2O \rightleftharpoons OH{\cdot}CHPh{\cdot}SH(OH){\cdot}CH_2Ph \rightleftharpoons \\ CHPh{:}S(OH){\cdot}CH_2Ph + H_2O \rightleftharpoons CH_2Ph{\cdot}S(OH)_2{\cdot}CH_2Ph \rightleftharpoons \\ CH_2Ph{\cdot}SO{\cdot}CH_2Ph + H_2O.\end{gathered}$$

There remains now only the description of some experiments performed with benzyl sulphoxide, some of which were suggested by its behaviour with hydrochloric acid, and some carried out with the view of obtaining additional evidence of its two-fold constitution.

Other Reactions of Benzyl Sulphoxide which throw Light on its Constitution.

Action of Sulphuric Acid on the Sulphoxide.—Concentrated sulphuric acid seems to have little or no action on the sulphoxide. On warming gently, the sulphoxide dissolves, and it can be recovered unaltered by pouring the solution into water. When heated at a high temperature with dilute (3 per cent.) acid, however, decomposition sets in. In a sealed tube at 170° the reaction is very slight, although the odour of mercaptan and benzaldehyde is distinct on opening the tube. At 200°, however, reaction is complete after eight hours' heating. There is no pressure on opening, which is an indication that destructive decomposition has not taken place, and the contents of the tube on steam-distillation yield a distillate composed chiefly of benzaldehyde, with a little mercaptan, and a non-volatile residue which can be resolved into benzyl disulphide and benzyl sulphide. From the original sulphoxide about one-third of the weight each of aldehyde and disulphide, and a little less than a third of sulphide, were obtained.

A small, but distinct, amount of hydrogen sulphide is also formed in this reaction. From these results it is clear that the sulphoxide has reacted with water just as it does with hydrochloric acid in equations *D* and *E*, the only two of the equations of reaction, it may be noted, in which no benzyl chloride is produced; further, to react as in these two equations, the sulphoxide must have been present both in the enolic and ketonic forms, and as the reaction took place without the agency of hydrochloric acid, additional evidence is thus afforded for the view adopted concerning the catalytic action of water.

Destructive Distillation of Benzyl Sulphoxide.—The experiments of Fromm and Achert (*Ber.*, 1903, **36**, 534) on this subject may be quoted here, because the ready formation of benzaldehyde led these investigators to doubt the usually accepted constitution of the sulphoxide. At 210° the pure sulphoxide decomposes, yielding benzyl disulphide, toluene, benzaldehyde, and sulphur dioxide. In discussing these results, Fromm and Achert say: "The remarkable decomposition of benzyl sulphoxide at 210°, and in particular the formation of benzaldehyde, raises doubt as to whether the constitutional formula $(C_6H_5\cdot CH_2)_2S{:}O$, ascribed to the sulphoxide, is the right one; if it be so, then transference of oxygen from sulphur to carbon must have taken place. Such an assumption is unnecessary if oxygen is combined with carbon in the sulphoxide in a manner expressed by the formula $C_6H_5\cdot CH_2\cdot S\cdot O\cdot CH_2\cdot C_6H_5$." The reduction of the sulphoxide with zinc and hydrochloric acid yields, however, benzyl sulphide, and not a mixture of benzyl mercaptan and benzyl alcohol, as would be expected with a compound of this constitution, so that the authors say, in conclusion, "Es muss also trotz der eigenartigen Zersetzung des Benzylsulfoxyds bei 210° bei der alten Formel bleiben."

It is hardly necessary to add that the enolic formula proposed in this paper represents the sulphoxide as containing oxygen combined directly with carbon, and thus in a favourable position for the formation of benzaldehyde on disruption of the sulphoxide molecule. The easy formation of sulphur dioxide, which is quite as remarkable in its way as that of benzaldehyde, would, on the other hand, be more natural to a compound having the ordinary ketonic structure of the sulphoxide; so far, then, as reactions of destructive decomposition of compounds throw light on their constitution, the results of the dry distillation of benzyl sulphoxide may be held to confirm the hypothesis of ketonic and enolic structure which has been advanced.

Action of Acetic Anhydride on Benzyl Sulphoxide.—The study of the action of hydrochloric acid on the sulphoxide having shown that, with increasing temperature and decreasing water-concentration, more and more sulphoxide reacts in the enolic form, and as this form tends to decomposition into benzaldehyde and benzyl mercaptan, as in equation *E*, it was thought that a complete resolution of the sulphoxide into its proximate constituents might be attainable by heating it with a dehydrating agent, especially as the condensation of these constituents under the influence of the dehydrating agent might be expected to take place and to be a factor in promoting the reaction. This influence has been justified by experiment. Fifteen grams of benzyl sulphoxide and 25 c.c. of acetic anhydride were heated in a sealed tube for five hours at 150°. There was no pressure on opening the tube. Steam distillation yielded an oil containing a trace of benzyl mercaptan, a considerable amount of benzaldehyde (which was separated with sodium hydrogen sulphite), and also of another liquid with a powerful mercaptan-like odour, which did not decolorise iodine. This liquid boils at a high temperature (about 250°) with slight decomposition, and does not solidify in a freezing mixture. Although it has not yet been obtained in a condition pure enough for analysis, hydrolytic experiments show that it is in all probability benzyl acetyl sulphide, $C_6H_5{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}CH_3$. The residue from the steam distillation on recrystallisation yielded pure benzaldehyde-benzylmercaptal (m. p. 61°), and was quite unmixed. The meaning of this reaction seems fairly clear. Under the combined influence of the high temperature and the dehydrating agent, the benzyl sulphoxide has become completely converted into the enolic form. It has then suffered rupture with formation of benzaldehyde and benzyl mercaptan, thus:

$$CH_2Ph{\cdot}S{\cdot}CHPh{\cdot}OH = Ph{\cdot}CHO + CH_2Ph{\cdot}SH.$$

These products have been condensed in part to the mercaptal:

$$Ph{\cdot}CHO + 2HS{\cdot}CH_2Ph = H_2O + CHPh(S{\cdot}CH_2Ph)_2,$$

the water being absorbed as soon as formed by the acetic anhydride. Apparently, also, some mercaptan has condensed with acetic anhydride, yielding benzyl acetyl sulphide:

$$2CH_2Ph{\cdot}SH + (CH_3{\cdot}CO)_2O = H_2O + 2CH_2Ph{\cdot}S{\cdot}CO{\cdot}CH_3,$$

and benzaldehyde has been left in excess from these two main reactions.

Action of Benzoyl Chloride on Benzyl Sulphoxide.—Additional evidence of the enolic form of the sulphoxide was sought for in the reaction with benzoyl chloride. There is no apparent reaction, however, when these compounds are brought together according to the Schotten-Baumann method, but when heated in presence of carbon tetrachloride complete decomposition of the sulphoxide is effected. Twenty-five grams of benzoyl chloride and 150 c.c. of carbon tetrachloride were heated for some hours in a reflux apparatus fitted with traps, so that any moisture present in the apparatus and materials was eliminated, and the hydrochloric acid produced was absorbed. After cooling, 20 grams of dry sulphoxide were added to the liquid. On again heating, a steady stream of hydrogen chloride was evolved, and this continued for about twelve hours. The contents of the flask were then shaken with small quantities of sodium hydroxide solution to decompose excess of benzoyl chloride, and distilled in a current of steam. Treatment of distillate and residue in the usual way yielded relatively large amounts of benzaldehyde and benzaldehyde-benzylmercaptal, and smaller quantities of benzyl disulphide, benzyl sulphide, and benzyl mercaptan, with possibly a little benzoyl benzyl sulphide, and apparently no benzyl chloride, or, at most, a trace. The reaction, in the main, thus resembles the foregoing one. Under the combined influence of the dehydrating agent and a moderately high temperature, the benzyl sulphoxide has become largely converted into the unstable enolic modification, which has decomposed into benzaldehyde and benzyl mercaptan. These have then condensed together to form benzaldehyde-benzylmercaptal, an equivalent of aldehyde remaining uncombined. The water eliminated in this reaction has decomposed some benzoyl chloride, and part of the hydrochloric acid produced thereby has reacted with the unaltered sulphoxide according to reaction *D* (and possibly to some extent, *E*), furnishing thus the disulphide and the sulphide, and setting free an additional quantity of benzaldehyde. The supply of benzaldehyde has further been supplemented by a small amount—equivalent to the mercaptan left uncombined in the first reaction of condensation.

The reaction therefore with benzoyl chloride, although it has failed to furnish the benzoyl benzyl sulphoxide, which it might have been expected to yield with a secondary alcohol of the constitution ascribed to the enolic form of benzyl sulphoxide, has nevertheless supplied evidence in favour of this constitution, and in harmony with the results of many other reactions which have been already described.

Some Miscellaneous Reactions.—For convenience sake, some properties and reactions of benzyl sulphoxide which have been noted and studied in the course of this work, but which have thrown little light on the main problem, may be mentioned here.

In the preparation of the sulphoxide by the oxidation of the sulphide with nitric acid (sp. gr. 1·3), a considerable quantity of benzaldehyde is always produced, no matter how pure the materials may be. Having regard to the instability of the enolic form of the sulphoxide, it was thought that this benzaldehyde might arise from the decomposition of the sulphoxide, and experiment shows this to be the case. This reaction is strikingly shown by chromic acid, for on gently warming a little sulphoxide with an aqueous solution of the acid in a test-tube, the odour of benzaldehyde is almost immediately observed.

The ready oxidation of the sulphoxide to sulphone by chromic acid and potassium permanganate in acetic acid solutions may again be partly conditioned by the ketonic structure of the compound in the solutions of that acid.

The small, although distinct, solubility of benzyl sulphoxide in water (roughly estimated as 0·4 per cent.), whereby it differs from the other sulphur compounds dealt with in this paper, may possibly be connected with its enolic structure.

The sulphoxide gives no colour reactions with ferric chloride, and apparently cannot be alkylated, nor does it seem to combine with phenylcarbimide, either at the ordinary temperature or when heated with it in chloroform solution in a sealed tube at 100° for twenty hours. It is impossible, however, to appraise the value of this negative evidence as yet.

The formulation of benzyl sulphoxide as a secondary alcohol ($OH\cdot CHPh\cdot S\cdot CH_2Ph$) has suggested its derivation by reduction of the corresponding ketone, benzoyl benzyl sulphide ($COPh\cdot S\cdot CH_2Ph$), and many experiments have been carried out with the view of proving this relationship. The ketone, however, is extremely unstable, and is reduced with disruption of the molecule even by mild reducing agents, the first products of decomposition being apparently benzaldehyde and benzyl mercaptan. This subject is still under investigation.

Conclusions.

To sum up the chief results of this investigation, the reactions of benzyl sulphoxide are best interpreted on the assumption that its structure is two-fold, the varieties differing in the disposition of the oxygen atom in the molecule, and being convertible into one another after the manner of dynamic isomerides. On the basis of the hypothesis of tautomerism proposed, it is possible to develop a series of equations representing the action of hydrochloric acid on each form (ketonic and enolic) of the sulphoxide, and on mixtures of the two forms, which not only give a clear account of the production of the many products in this somewhat complicated reaction, but also enable the hypothesis to be tested, by comparison of the quantitative data of reaction with the results calculated from these equations. The agreement of experimental with calculated values in each of twelve reactions, carried out under different conditions, may be held to justify the hypothesis.

The quantitative data enable the equilibrium between the two forms to be determined under certain specified conditions, and the conclusion is reached that this equilibrium is dependent chiefly on the temperature and the concentration of water in the solvent. Increase of temperature and decrease of water-concentration favour the existence of the enolic modification.

The enolic form is comparatively unstable, and, on breaking up, yields benzaldehyde and benzyl mercaptan; these products, or derivatives of them, are thus formed with ease when the sulphoxide is placed under conditions favourable to the development of the enolic modification, for example, when heated with dehydrating agents like acetic anhydride and benzoyl chloride.

Finally, this case of tautomerism is peculiar in that change from one form to another involves the transposition of the oxygen atom in the molecule.

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XLVI.—*The Nature of Ammoniacal Copper Solutions. Part II. The Solubility of Cupric Hydroxide in Ammoniacal Sulphate Solutions.*

By HARRY MEDFORTH DAWSON.

IN a previous paper (Trans., 1906, **89**, 1666; compare also Trans., 1900, **77**, 1239) it has been shown by measurements of the distribution of ammonia between ammoniacal copper sulphate solutions and chloroform that the copper in such solutions is present for the most part in the form of the complex radicle $Cu \cdot 4NH_3$. On dilution of the solution or diminution of the concentration of the ammonia relatively to that of the copper, the equilibrium between the components of the solution is displaced in such a way that the ratio of the combined ammonia to copper diminishes. The ultimate result of the displacement is a precipitation of copper from solution in the form of cupric hydroxide. Further information relating to the nature of ammoniacal copper solutions has been sought by a study of the solutions which are obtained when ammoniacal ammonium sulphate solutions are saturated with cupric hydroxide.

It is well known that definite modifications of many of the slightly soluble metallic hydroxides are not at all readily obtained. This is probably connected with the fact that the precipitated hydroxides are frequently only obtainable in the form usually described as amorphous, and the numerous discrepancies which are to be found in the literature dealing with the solubility relationships of metallic hydroxides are no doubt attributable in a large measure to the existence of several forms of such amorphous hydroxides.

Cupric hydroxide can be obtained in three different forms: crystalline, amorphous, and colloidal. The colloidal modification, which is extremely difficult to obtain in a pure condition, is very unstable, and its properties depend to a very considerable extent on the temperature of the solution from which it is precipitated, on the length of time it is kept in contact with water, and on other circumstances (compare Spring and Lucion, *Zeitsch. anorg. Chem.*, 1892, **2**, 195; van Bemmelen, *ibid.*, 1894, **5**, 466). In contrast with the other forms of cupric hydroxide, the hydrogel acts more or less readily on aqueous solutions of the alkali bromides and iodides with the formation of basic cuprous halides and evolution of oxygen.

Preparations of what under the microscope appears to be amorphous cupric hydroxide are much more stable than the colloidal form. These amorphous modifications, obtained from ammoniacal solutions of copper salts by the addition of dilute alkali hydroxide or of large quantities of water, or by the action of dilute alkali on a solution of cupric ammonium chloride, or, further, by diluting largely the solution which is obtained by the action of air on metallic copper and ammonia solution, are, according to van Bemmelen, not equally stable. Under the influence of boiling water some preparations remain unchanged, whilst others exhibit colour changes to a greater or less extent. Two samples of cupric hydroxide, precipitated under exactly the same conditions by the addition of alkali hydroxide to an ammoniacal copper sulphate solution, were found by Bonsdorff (*Zeitsch. anorg. Chem.*, 1904, **41**, 132) to exhibit considerable differences in respect of their solubility in ammonia solutions.

Crystalline cupric hydroxide has been obtained in different ways by Becquerel (*Compt. rend.*, 1852, **34**, 573), Böttger (*Jahresber.*, 1858, 198), Péligot (*Compt. rend.*, 1861, **53**, 209), and by van Bemmelen (*loc. cit.*, p. 474). The crystalline hydroxide can be heated at 100° in air or under water without change of colour. The definiteness of character conferred on the substance by its crystalline form was perhaps the principal reason for deciding that the experiments to be described in this paper should be carried out with crystalline cupric hydroxide. It is by no means certain that the same crystalline modification is obtained by the various methods of preparation referred to above, but this is not of much importance for the purpose of this investigation. The chief desideratum was the possibility of preparing a definite modification at will, and the method actually adopted is practically identical with that of Böttger (*loc. cit.*).

The process consisted in adding aqueous ammonia from a burette to a boiling and well-stirred solution containing 50 grams of copper sulphate dissolved in 300—400 c.c. of water until the supernatant liquid began to assume the deep blue colour of an ammoniacal copper solution; the precipitated green basic salt was well washed and triturated in a porcelain dish with 300—400 c.c. of a 6 per cent. solution of sodium hydroxide free from carbonate, and the blue hydroxide into which it is thereby converted was dried in a vacuum over sulphuric acid, after having been washed with distilled water until every trace of sulphate had been removed. The crystalline hydroxide obtained in this way retains its bright blue colour for a very long time at the ordinary temperature, and is not at all readily converted into the oxide at 100°.

As the most convenient method of identifying a particular modification of the hydroxide, the solubility was determined. The solubility of cupric hydroxide in water is far too small for direct measurement, and as solvent an aqueous solution containing 1 mol. ammonia per litre was employed.

As a test of the stability of the hydroxide prepared as described, the solubility of the freshly-prepared substance and that of the same preparation which had been kept in a stoppered bottle for more than a year were compared. In 1-molar ammonia at 18°, the values were identical. The definite character of the product is, moreover, indicated by the following numbers, which represent the solubilities of a series of different preparations of the substance in $1N$-ammonia at 18°: 0·0108, 0·0109, 0·0110, 0·0109, and 0·0108 mol. per litre. Of the various preparations, all but one retained the original bright blue colour when kept in stoppered bottles for a year. In the exceptional case, the colour changed to a bluish-green after some months, but in spite of this the solubility in $1N$-ammonia remained unchanged.*

The bright blue hydroxide, prepared as described above, dissolves readily in aqueous ammonia, equilibrium between solid and solution being attained in a comparatively short time. The addition of ammonium sulphate to a given ammonia solution increases the solubility of the hydroxide to a marked extent; within certain limits the increase in the solubility is approximately proportion l to the quantity of ammonium sulphate added.

With the object of obtaining information in regard to the nature of ammoniacal copper sulphate solutions, the dependence of the solubility on the ammonia and ammonium sulphate concentrations has been investigated. Although, in the first instance, a comparatively small number of experiments was planned, the difficulty of drawing any very definite conclusions from the experimental data necessitated the carrying out of a much larger series of measurements.

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* Specimens which had not apparently changed at the end of a year have all been found to undergo very pronounced colour changes at the end of two or three years.

The ammonia used in these experiments was prepared by distilling an ammonia solution (0·88 sp. gr.) to which sodium hydroxide was added in a slow current of air free from carbon dioxide, the ammonia gas evolved being collected in well-cooled conductivity water. The ammonium sulphate was purified by repeated crystallisation.

The solubility data are recorded in table I. The numbers represent the number of gram-atoms of copper per litre, the temperature of the measurements being 18°. The complete series of experiments represents a variation in the ammonia concentration of 0·05 to 5 mols. per litre, and in the ammonium sulphate concentration of 0·01 to 0·4 mols. per litre. The ammonia and ammonium sulphate concentrations registered in the first vertical and the top horizontal column respectively are the concentrations of the solutions before saturation with cupric hydroxide. In the saturated solutions the sulphate and ammonia concentrations are slightly smaller because of the increase in volume which accompanies solution of the hydroxide; it has not, however, been considered necessary to take account of these small volume changes.

TABLE I.

Solubility of Cupric Hydroxide in Ammoniacal Ammonium Sulphate Solutions.

Mols. NH_3 per litre	Mols. $(NH_4)_2SO_4$ per litre.						
	0	0·01	0·025	0·05	0·1	0·2	0·4.
0	—	—	—	(0·0004)	—	(0·0157)	(0·0180)
0·05	—	0·00129	0·00511	(0·0130)	(0·0215)	(0·0325)	(0·0579)
0·1	—	0·00326	0·0108	0·0233	(0·0411)	—	—
0·2	0·00051	0·00649	0·0175	0·0384	0·0690	(0·1027)	(0·1397)
0·5	0·0033	0·0127	0·0284	0·0536	0·1013	0·1844	(0·2805)
1·0	0·0109	0·0210	0·0386	0·0660	0·1185	0·2275	0·4135
2·0	0·0314	0·0462	0·0605	0·0886	0·1468	0·2591	0·4718
3·0	0·0548	0·0672	0·0847	0·1156	0·1740	0·2861	0·5044
4·0	0·0784	0·0922	0·1101	0·1397	0·2002	0·3188	0·5451
5·0	0·1041	0·1154	0·1320	0·1639	0·2239	0·3415	0·5615

The numbers in brackets are data which were obtained under the same conditions as the other experimental numbers; but it is quite certain that they do not represent the solubility of cupric hydroxide in the corresponding solutions, and improbable that they correspond with any definite equilibrium condition. After being agitated for some time with 0·2- and 0·4-molar ammonium sulphate solutions containing little or no free ammonia, the blue hydroxide was found to have changed to a green colour in consequence of the formation of a basic salt. It is not possible to say what exactly is the lower limit of the ammonia concentration at which this change no longer takes place, but it was not observed in the case of solutions containing two or more mols. of ammonia per mol. of ammonium sulphate. Solutions containing a relatively smaller proportion of ammonia than this are eliminated in the following theoretical consideration of the solubility data.

From the small solubility of the hydroxide in ammonia-free ammonium sulphate solutions, it appears possible to draw a conclusion of some importance. If a cupriammonia complex of the formula $Cu\cdot 2NH_3$ were capable of existence, this would presumably undergo dissociation to a very much smaller extent than the tetra-ammonia complex, and it might be expected that cupric hydroxide in contact with ammonium sulphate solutions would give rise to the corresponding cupriammonia sulphate according to the equation:

$$Cu(OH)_2 + (NH_4)_2SO_4 = Cu\cdot 2NH_3SO_4 + 2H_2O.$$

The small amount of copper which is found in such solutions is, however, unfavourable to the view that a cupri-diammonia compound is formed. The copper present in the solutions is, on the other hand, apparently due to the transformation of the hydroxide into a basic salt, whereby ammonia is liberated. By the interaction of the ammonia thus set free with copper hydroxide and ammonium sulphate, cupritetra-ammonia sulphate is formed. A knowledge of the composition of the green basic salt is unnecessary for the present consideration, and if, for example, we assume that it corresponds with the simplest possible formula, $Cu_2(OH)_2SO_4$, the changes taking place may be represented by the equations:

$$2Cu(OH)_2 + (NH_4)_2SO_4 = Cu_2(OH)_2SO_4 + 2NH_3 + 2H_2O.$$
$$Cu(OH)_2 + 2NH_3 + (NH_4)_2SO_4 = Cu\cdot 4NH_3SO_4 + 2H_2O.$$

The behaviour of cupric hydroxide towards ammonium sulphate solutions containing little or no free ammonia thus leads to the view that a cupri-diammonia complex either does not exist or is not readily formed, and in the further consideration of the previous table it will be assumed that the dissolved copper is present in the solutions in the form of the tetra-ammonia complex.* Since ammonium sulphate appears to have no direct solvent action on cupric hydroxide, it is extremely probable that the passage of copper into solution is primarily determined by the ammonia, cupritetra-ammonia hydroxide being the initial product. This cupriammonia hydroxide then reacts with the ammonium sulphate according to the equation:

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* From an examination of solutions of cupric hydroxide in ammonia by the distribution method (Trans., 1900, **77**, 1255), Dawson and McCrae drew the conclusion that the cupriammonia base corresponds with the formula $Cu\cdot 2NH_3(OH)_2$. Later work has shown that the solutions examined were supersaturated with respect to cupric hydroxide, and on this account the experimental data cannot be utilised to draw conclusions relating to the nature of the complex base.

$$Cu{\cdot}4NH_3(OH)_2 + (NH_4)_2SO_4 = Cu{\cdot}4NH_3SO_4 + 2NH_4OH,$$

the change consisting simply in the displacement of the ammonia from its sulphate by the stronger cupriammonia base.

If the displacement is sensibly complete and there are no secondary disturbing factors to be taken into account, then, according to this view, the saturated solution should contain one gram-atom of copper for each mol. of ammonium sulphate originally present, two mols. of ammonia being simultaneously used up in formation of the tetra-ammonia compound. If the original solution contained n mols. of ammonia per mol. of ammonium sulphate, $n - 2$ mols. should still be available for dissolving cupric hydroxide. According to this, the concentration of copper in a solution which contained originally n mols. of ammonia and m mols. of ammonium sulphate per litre should be given by the equation $c = c_1 + m$, where c_1 is the concentration of copper in a $(n - 2m)$ molar ammonia solution when saturated with cupric hydroxide.

This equation may be written in the form $\frac{c - c_1}{m} = 1$, and in order that the experimental data may be compared with the requirements of the equation, the values of $\frac{c - c_1}{m}$ are recorded in table II. Solutions for which n is less than $2m$ are, of course, omitted.

TABLE II.

Values of $\frac{c - c_1}{m}$.

	Mols. $(NH_4)_2SO_4$ per litre.					
Mols. NH_3 per litre.	0·01	0·025	0·05	0·1	0·2	0·4
0·05	0·13	0·20	—	—	—	—
0·1	0·33	0·43	0·47	—	—	—
0·2	0·61	0·69	0·77	0·69	—	—
0·5	0·95	1·02	1·03	1·00	0·92	—
1·0	1·02	1·14	1·13	1·11	1·11	1·03
2·0	1·48	1·18	1·18	1·19	1·18	1·14
3·0	1·32	1·24	1·26	1·24	1·20	1·17
4·0	1·42	1·31	1·27	1·27	1·25	1·21
5·0	1·20	1·17	1·25	1·24	1·24	1·19

It is evident that the value of $\frac{c - c_1}{m}$ for the more dilute ammonia solutions is considerably less than unity, and increases with increasing ammonia concentration. For ammonia solutions containing more than one mol. per litre, $\frac{c - c_1}{m}$ is, on the other hand, greater than unity, and varies more or less irregularly about a mean value of 1·20, which appears to be more or less independent of the ammonium sulphate concentration.

The differences exhibited by the values of $\frac{c-c_1}{m}$ can be shown to be due to the operation of certain disturbing factors. In the first place, it is improbable from considerations of affinity and mass action that the displacement of ammonium hydroxide by cupriammonia hydroxide is complete; what we have to deal with is an equilibrium condition corresponding with the scheme:

$$Cu\cdot 4NH_3(OH)_2 + (NH_4)_2SO_4 \rightleftarrows Cu\cdot 4NH_3SO_4 + 2NH_4OH.$$

The sulphuric acid is distributed between the two competing bases in proportions determined by their relative affinities and active masses, and the relationship between the active masses is known approximately from the measurements of the solubility of cupric hydroxide in pure ammonia solutions. In consequence of the rapid increase in the solvent power of ammonia for cupric hydroxide as the ammonia concentration increases from 0 to 1 mol. per litre, the equilibrium in the solution will be displaced to the right with increasing ammonia concentration, and to the left as the ammonia concentration is decreased. The lower values of $\frac{c-c_1}{m}$ found for the more dilute ammonia solutions are thus readily explained.

The higher values found in the case of the more concentrated ammonia solutions—values which exceed what would appear to be the limiting maximum value corresponding with the complex displacement of the ammonia from the sulphate by the cupriammonia base—are due to an entirely different cause. Corresponding with this, it should be observed that the mode of variation of $\frac{c-c_1}{m}$ with the ammonia concentration is quite different in the case of the more concentrated ammonia solutions from that found in the dilute solutions.

If a solution which contained originally n mols. of ammonia and m mols. of ammonium sulphate per litre (and which, therefore, in the case of complete displacement of the ammonia from the sulphate by the cupriammonia base would yield m mols. of cupriammonia sulphate and $n-2m$ mols. of free ammonia per litre) is compared with a sulphate-free ammonia solution of concentration $n-2m$ mols. per litre, a difference is to be noted, which accounts for the higher values of $\frac{c-c_1}{m}$. In presence of the cupriammonia ions resulting from the dissociation of the cupriammonia sulphate, the extent to which the corresponding hydroxide is ionised will be appreciably less than in sulphate-free solution.

Since the ionic concentration product, $[Cu^{\cdot\cdot}].[OH']^2$, is constant for saturated solutions, the effect of the iso-ionic action will be to diminish the concentration of the OH′ ion and therefore to increase the solubility of cupric hydroxide in a solution containing a given amount of free ammonia. This increased solubility obviously corresponds with the higher values of $\frac{c - c_1}{m}$ found in the case of the more concentrated ammonia solutions.

Experimental evidence in support of this explanation has been obtained by measurements of the solubility of cupric hydroxide in ammonia solutions containing variable amounts of barium and sodium hydroxides.

The barium hydroxide used was purified by repeated crystallisation, and the stock solution of sodium hydroxide was obtained by the action of sodium on water in a carbon dioxide-free atmosphere. The solubility data are recorded in table III. In the case of barium hydroxide, the numbers, not only show the influence of increasing quantities of the hydroxide on the solubility in a given ammonia solution, but also the effect of a constant quantity of barium hydroxide when the ammonia concentration is varied.

TABLE III.

Solubility of $Cu(OH)_2$ *in Ammoniacal* $Ba(OH)_2$ *and* NaOH *Solutions.*

Solvent.	Copper concentration (gram-atoms per litre).
1 mol. NH_3 + 0 mol. $Ba(OH)_2$	0·0109
,, + 0·0025 ,,	0·00907
,, + 0·005 ,,	0·00801
,, + 0·01 ,,	0·00633
,, + 0·02 ,,	0·00526
2 mols. NH_3 + 0 mol. $Ba(OH)_2$	0·0314
,, + 0·01 ,,	0·0277
4 mols. NH_3 + 0 mol. $Ba(OH)_2$	0·0784
,, + 0·01 ,,	0·0747
1 mol. NH_3 + 0 mol. NaOH	0·0109
,, + 0·01 ,,	0·00766
,, + 0·02 ,,	0·00655
,, + 0·03 ,,	0·00531
,, + 0·05 ,,	0·00456
,, + 0·10 ,,	0·00410

An inspection of the numbers in the table shows that the solubility of cupric hydroxide in ammonia solutions containing the largely ionised barium or sodium hydroxides is considerably less than in pure ammonia solutions. The difference in solubility increases with the concentration of the alkali or alkaline-earth hydroxide, and this is to be attributed chiefly to the increase in the OH′ ion concentration—the product $[Cu^{\cdot\cdot}].[OH']^2$ must be constant—and to a smaller extent to the "salting-out" action of the dissolved hydroxide.

Since increase in the OH′ ion concentration diminishes the solubility of the cupric hydroxide, it is legitimate to conclude that the diminution in the OH′ ion concentration, which results from the iso-ionic action of cupritetra-ammonia sulphate on the corresponding base, will increase the solvent power of $(n-2m)$ molar ammonia for cupric hydroxide in comparison with the solvent power of a pure ammonia solution containing $(n-2m)$ mols. per litre.

The values of $\frac{c-c_1}{m}$ recorded in table II are thus seen to be explainable on the assumption of an equilibrium condition corresponding with the reversible change:

$$\mathrm{Cu\cdot 4NH_3(OH)_2 + (NH_4)_2SO_4 \rightleftharpoons Cu\cdot 4NH_3SO_4 + 2NH_4OH.}$$

The results obtained in the measurements of the combined ammonia in ammoniacal copper sulphate solutions by the distribution method (*loc. cit.*) are in agreement with this theory of the nature of such solutions, which, moreover, explains the fact that cupric hydroxide is precipitated when the solutions are sufficiently diluted.

Strength of Cupritetra-ammonia Hydroxide.—From the extent to which ammonia is displaced from its sulphate by the cupriammonia base, as indicated by the solubility data in table I and the values of $\frac{c-c_1}{m}$ in table II, it is evident that the complex hydroxide is a much stronger base than ammonia. In order to obtain further information with regard to the strength of the cupriammonia base, measurements of the solubility of cupric hydroxide in ammonia solutions containing sodium sulphate have been made. The data are recorded in table IV. Under $\mathrm{Cu_1}$ are given the copper-concentrations in gram-atoms per litre for a series of such solutions, and for comparison the values for the corresponding ammoniacal ammonium sulphate are placed alongside under $\mathrm{Cu_2}$.

TABLE IV.

Solubility of $\mathrm{Cu(OH)_2}$ *in Ammoniacal Sodium Sulphate Solutions.*

1-Molar ammonia.			4-Molar ammonia.		
$\mathrm{Na_2SO_4}$ mols. per litre.	$\mathrm{Cu_1}$.	$\mathrm{Cu_2}$.	$\mathrm{Na_2SO_4}$ mols. per litre.	$\mathrm{Cu_1}$.	$\mathrm{Cu_2}$.
0	0·0109	0·0109	0	0·0784	0·0784
0·025	0·0134	0·0386			
0·1	0·0162	0·1185	0·1	0·0994	0·2002
0·2	0·0192	0·2275	0·2	0·1161	0·3188

It is evident that the presence of sodium sulphate in the solution increases the solubility of the cupric hydroxide, although the increase produced by a given quantity of sodium sulphate is very small compared with that brought about by an equivalent quantity of ammonium sulphate. The increase caused by the presence of the sodium sulphate expressed in terms of that brought about by an equivalent amount of ammonium sulphate is for the three 1-molar ammonia solutions 8·4, 4·8, and 3·8 per cent. respectively, and for the 4-molar ammonia solutions 17 and 16 per cent. respectively. These numbers indicate that the displacement of sodium hydroxide from the sulphate by the cupriammonia base takes place to only a small extent; from this it may be inferred that cupriammonia hydroxide, although a much stronger base than ammonia, is weak in comparison with the alkali and alkaline-earth hydroxides. The same conclusion follows from a comparison of the electrical conductivities of corresponding ammoniacal solutions of cupric and barium hydroxides.

The results of the solubility measurements recorded in table I may now be compared with the data furnished by the distribution experiments (previous paper, *loc. cit.*). From the solubility numbers it is possible by interpolation to deduce approximately the ammonia concentration which is necessary to dissolve cupric hydroxide in such quantity that the resulting solution contains copper and sulphate in equivalent proportions. Such a solution is obviously identical with that which would be obtained by adding the requisite quantity of ammonia to a copper sulphate solution. If in accordance with the equation

$$Cu(OH)_2 + (NH_4)_2SO_4 + nNH_3 = Cu{\cdot}4NH_3SO_4 + (n-2)NH_3 + 2H_2O$$

n mols. of ammonia are required per mol. of cupric hydroxide (or ammonium sulphate), it is obvious that the molar ratio of ammonia to copper in the resulting solution is equal to $n+2$. In table V the approximate (interpolated) values of $n+2$ for a series of solutions of gradually increasing concentration are recorded.

TABLE V.

$Cu = SO_4$ concentration.	$n+2$.
0·01 mol. per litre..................	35
0·025 ,, ,, ...	18
0·05 ,, ,, ...	11
0·1 ,, ,, ...	7
0·2 ,, ,, ...	5·2

With increasing concentration, the molar ratio of ammonia to copper diminishes, but even in the most concentrated solution it is considerably greater than four, the value corresponding with a solution such as would be obtained by dissolving the crystalline salt, $Cu{\cdot}4NH_3SO_4,H_2O$, in water. It follows, therefore, that solutions of this substance containing 0·1, 0·2, and probably also 0·4 mol. per litre are supersaturated with respect to cupric hydroxide. This is also the case for all ammoniacal copper sulphate solutions for which the molar ratio of ammonia to copper is less than that corresponding with the $n+2$ values in the preceding table.

Many of the solutions for which the ratio between combined ammonia and copper was determined by distribution measurements (*loc. cit.*) are therefore supersaturated with regard to cupric hydroxide. These solutions, it may be noted, were prepared by the addition of ammonia to copper sulphate solutions, and although during this process a precipitate is inevitably formed, this appears to dissolve completely, giving optically clear solutions which are apparently quite stable in spite of the fact that the ratio of ammonia to copper is considerably smaller than corresponds with the values in table V.

For the purpose of comparing more exactly the solubility and distribution data, a particular solution may be considered. From crystallised cupriammonia sulphate a 0·1-molar solution can be prepared which is, initially, optically clear (compare Horn and Taylor, *Amer. Chem. J.*, 1904, **32**, 253). Measurement of the ratio of combined ammonia to copper in the freshly-prepared solution gave the value 3·45. On the assumption that no complex radicle containing less than 4 mols. ammonia per atom of copper is formed, it follows from this ratio that the solution contains 0·014 gram-atom of copper per litre which is uncombined with ammonia. The small value of the ionic solubility product $[Cu^{\cdot\cdot}].[OH']^2$ precludes the possibility that this amount of copper is present in solution in the form of cupric ions, and the conclusion seems inevitable that the copper which is not combined with ammonia is present in the form of colloidal cupric hydroxide. The fraction present in this form represents 14 per cent. of the total copper. On this view, the slow precipitation which takes place when the above solution is allowed to stand can be readily understood.

Also in agreement with this view is the fact that optically clear and apparently stable solutions, prepared by the addition of ammonia to solutions of copper sulphate, deposit cupric hydroxide when brought into contact with this substance, provided that the relative proportion of ammonia does not exceed a certain limit. Observations made with a solution of the composition 0·1-molar $(CuSO_4 + 4{\cdot}5NH_3)$ may be recorded in this connexion.

After shaking with cupric hydroxide for three days, the solution was found to contain only 0·083 gram-atom of copper per litre; further shaking for a period of four days produced no alteration in the copper content. About 17 per cent. of the original copper had therefore been deposited in the form of cupric hydroxide. Measurement of the ratio of combined ammonia to copper in the original solution gave the value 3·50. On the assumption that $Cu{\cdot}4NH_3$ represents the only cupriammonia complex which is contained in the solution, it follows from this ratio that about 12·5 per cent. of the copper is present in the uncombined condition. The two numbers, which represent respectively the proportion of copper deposited when the solution is brought into contact with cupric hydroxide and that of the copper which is not combined with ammonia, are not identical; this is probably due to the fact that the two data are not strictly comparable, for the separation of copper from solution in the former case necessitates a re-adjustment of the proportions of the components which take part in the equilibrium which is characteristic of these solutions.

The above comparison is sufficient to show that the results obtained by two entirely different methods of investigation are in substantial agreement. Whilst the author's distribution measurements led to the determination of the chemical dissociation of the cupriammonia complex which forms the chief constituent of the deep blue ammoniacal solutions of copper salts, the work communicated in this paper throws a great deal of light on the relationship between the several components which are in a condition of equilibrium in these solutions.

Addendum.—In a recent communication by Hantzsch and Robertson (*Ber.*, 1908, **41**, 4328), the nature of ammoniacal solutions of copper salts has been investigated by an optical method. An analysis of this method shows that it is not at all adapted for the quantitative determination of the extent to which dissociation of the cupriammonia complex takes place in a given solution; it is therefore not surprising to find that the results which I have obtained by a more trustworthy method (the distribution method) are subjected to criticism. The experimental material communicated in this paper is a fitting and sufficient reply to the critical observations of Hantzsch and Robertson.

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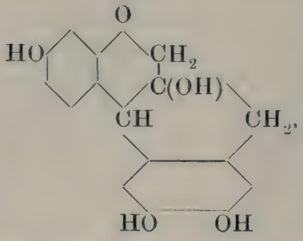
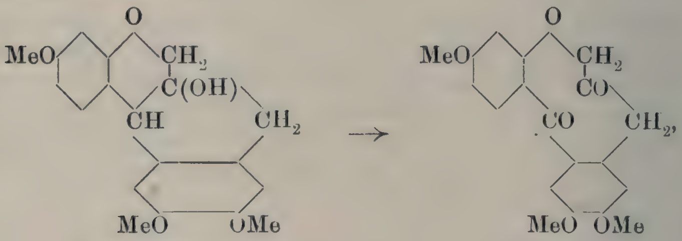
XLVII.—*Brazilin, Haematoxylin, and their Derivatives. Part X. The Constitution of Trimethylbrazilone, of α- and β-Anhydrotrimethylbrazilone, and of the corresponding Haematoxylin Derivatives.*

By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON
(1851 Exhibition Scholar).

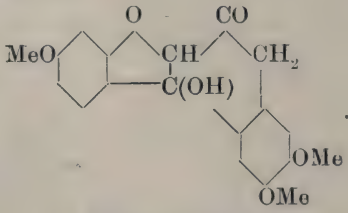
IN Parts VIII and IX of this research (Trans., 1908, **93**, 489, 1115) we have brought forward evidence which, in our opinion, clearly proves that the constitution of brazilin must be represented by the formula :



and it is there shown that this formula accounts in a comparatively simple manner for all the known reactions and decompositions of brazilin, trimethylbrazilin, and brazilein. In discussing trimethylbrazilone, one of the most important derivatives of brazilin, it was, however, found necessary to assume a rather complex series of molecular changes in order to derive a constitution which would account for the remarkable properties of this substance. It was suggested (*loc. cit.*, p. 498) that, during the oxidation of trimethylbrazilin to trimethylbrazilone, the central linking suffers disruption with the formation of an unstable diketone, which then undergoes internal condensation.



Trimethylbrazilin. Diketone.

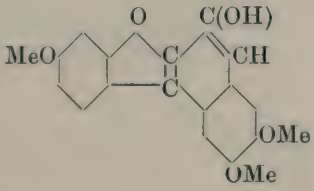


Trimethylbrazilone.

Before bringing our experiments on brazilin and hæmatoxylin to a conclusion, we thought it necessary still more thoroughly to investigate trimethylbrazilone in order to obtain further evidence which would leave no doubt as to its constitution and relationship to brazilin. Trimethylbrazilone is obtained from trimethybrazilin by oxidation with chromic acid, when the following change takes place:

$$\underset{\text{Trimethylbrazilin.}}{C_{19}H_{20}O_5} + O_2 = \underset{\text{Trimethylbrazilone.}}{C_{19}H_{18}O_6} + H_2O.$$

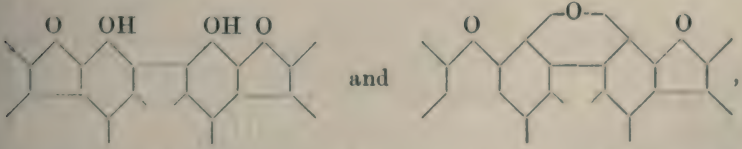
When trimethylbrazilone is treated with dehydrating agents, it is converted, with loss of water, into α-anhydrotrimethylbrazilone, $C_{19}H_{16}O_5$, a substance which contains a hydroxyl group, since it is converted into acetyl-α-anhydrotrimethylbrazilone by treatment with acetic anhydride. We have suggested that the elimination of water from trimethylbrazilone takes place in a simple manner, and that the formula:



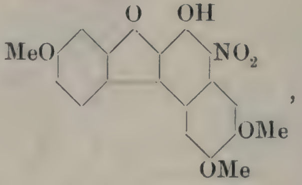
represents α-anhydrotrimethylbrazilone. According to this view, α-anhydrotrimethylbrazilone is a derivative of β-naphthol with one α-position free, and, in support of this, we showed that it possesses several of the properties characteristic of β-naphthol.

Thus, for example, it dissolves in dilute alkalis, and the solution combines with diazonium chlorides, yielding dyestuffs which are exactly similar to those produced in alkaline solutions of β-naphthol. We have continued our experiments in this direction (compare p. 391), and have prepared a number of interesting new derivatives of α-anhydrotrimethylbrazilone, the properties and decompositions of which afford further evidence that our view of the constitution of this substance is the correct one.

When α-anhydrotrimethylbrazilone is treated with ferric chloride, it is oxidised with formation of *di-α-anhydrotrimethylbrazilone*, and this substance is converted by phosphoryl chloride into the corresponding oxide. Using the central portion of the formulæ only:

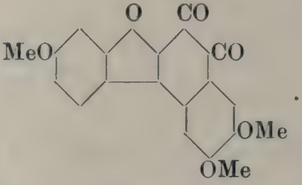


it is seen that these changes are exactly similar to the conversion of β-naphthol into β-dinaphthol and β-naphthylene oxide under the same conditions. Nitric acid reacts readily with acetyl α-anhydrotrimethylbrazilone, with the formation of the acetyl derivative of *nitro-a-anhydrotrimethylbrazilone*,

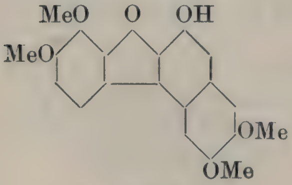


and several derivatives of this substance have been prepared and are described in detail in the experimental part of this paper.

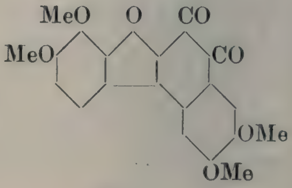
One of its most interesting reactions is its reduction by zinc dust and hydrochloric acid to the corresponding amino-derivative, which, when oxidised by ferric chloride, yields *trimethoxy-a-brazanquinone* (p. 394),



That this is an ortho-quinone is shown by its behaviour with *o*-tolylenediamine, with which it condenses with formation of a characteristic quinoxaline; on reduction, the quinone is converted into the corresponding dihydroxy-derivative, the diacetyl derivative of which is described on p. 396. Results exactly similar to those just described were obtained in the case of α-anhydrotetramethylhæmatoxylone (I).



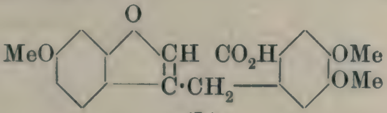
(I.)

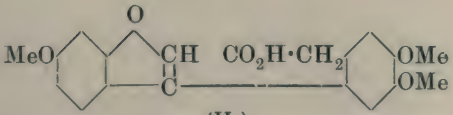


(II.)

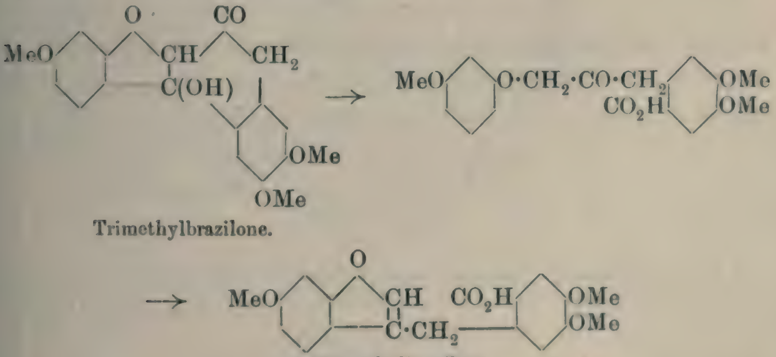
Nitric acid converts the acetyl derivative of this substance into *nitroacetyl-a-anhydrotetramethylhaematoxylone*, and this is readily reduced to the amino-derivative, which, on oxidation with ferric chloride, yields *tetramethoxy-a-brazanquinone* (II).

The investigation of the nature and constitution of the substances called ψ- and β-trimethylbrazilone and ψ- and β-tetramethylhæmatoxylone has proved to be a matter of very considerable difficulty. In 1904 (*Ber.*, **37**, 631) Herzig showed that trimethylbrazilone undergoes isomeric change when it is dissolved in sulphuric acid, and is converted into a new substance, called by him ψ-trimethylbrazilone. In a previous communication (Trans., 1908, **93**, 501) we described the results of a preliminary examination of this substance, during which we found that this carboxylic acid on oxidation with permanganate yielded large quantities of 2-carboxy-4 : 5-dimethoxyphenylacetic acid, $(MeO)_2C_6H_2(CO_2H)\cdot CH_2\cdot CO_2H$. These and other considerations led us to suggest two possible expressions for ψ-trimethylbrazilone, namely :


(I.)

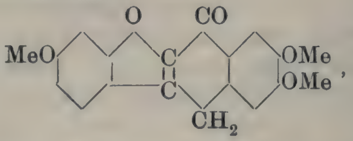

(II.)

The evidence available at that time was not sufficient to allow of a decision between these formulæ, but, as the result of further experiments (pp. 400—407), we are now in a position to show that formula (I) correctly represents the constitution of ψ-trimethylbrazilone. Before doing so it may be pointed out that this expression is readily derived from that of trimethylbrazilone by the following scheme of addition and subsequent elimination of water :

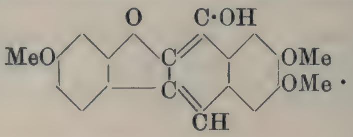

Trimethylbrazilone.

ψ-Trimethylbrazilone.

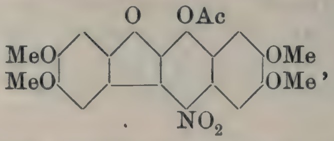
When ψ-trimethylbrazilone is treated with dehydrating agents, it loses the elements of water and is converted into β-anhydrotrimethylbrazilone. On the assumption that the above formula (I) is the correct expression for ψ-trimethylbrazilone, the most likely mechanism of this remarkable and interesting change is elimination of water between the carboxyl group and the >CH group of the coumarone ring, leading to the expression



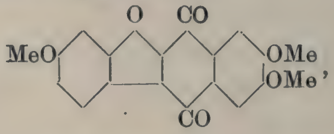
which, by intramolecular change, would then become



This formula represents β-anhydrotrimethylbrazilone as a derivative of α-naphthol with the second α-position free, and this view has been confirmed by further experimental investigation, since it has been found that, in its behaviour with diazo-solutions (p. 391) and in other respects, it exhibits properties exactly similar to those of α-naphthol. When acetyl-β-anhydrotrimethylbrazilone is treated with nitric acid, it yields *nitroacetyl-β-anhydrotrimethylbrazilone*,



and this, on reduction and subsequent treatment with nitrous acid, is converted into *trimethoxy-β-brazanquinone*,[*]



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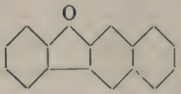
[*] The name "brazan" was given to the substance

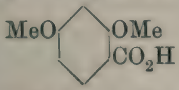


by Kostanecki and Lloyd (*loc. cit.*; compare Bolina, Kostanecki, and Tambor, *Ber.*, 1902, **35**, 1675). When trimethylbrazilone is heated with hydriodic acid it yields, in the first place, tetrahydroxybrazan, which undergoes further reduction to trihydroxybrazan, and the latter, when distilled with zinc dust, yields brazan. The explanation of this process is obviously as follows: Trimethylbrazilone is first converted by the action of the hydriodic acid into ψ-trimethylbrazilone, which loses a para-quinone which had already been obtained by Kostanecki and Lloyd (*Ber.*, 1903, **36**, 2194) from β-anhydrotrimethylbrazilone by oxidation with chromic acid.

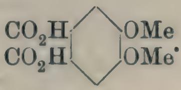
During the course of our experiments on ψ-trimethylbrazilone, we investigated its behaviour with potassium hypobromite, and obtained a new series of derivatives, the examination of which has served to confirm our views as to the constitution of this substance.

When ψ-trimethylbrazilone is treated with potassium hypobromite in the cold, it yields a bromolactone, $C_{18}H_{15}O_6Br$, which, when digested with chloroform, readily loses hydrogen bromide with formation of a lactone, $C_{18}H_{14}O_6$. The bromolactone, $C_{18}H_{15}O_6Br$, is readily hydrolysed by alkalis, and the monobasic acid which is produced again readily yields a lactone, $C_{18}H_{16}O_7$. This latter substance contains a phenolic hydroxyl group, since it gives a violet coloration with ferric chloride, and is converted by methylation into a methyl ether, $C_{18}H_{15}O_7Me$, which is itself a lactone.

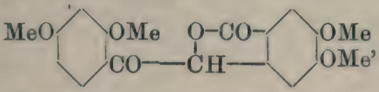
Important evidence bearing on the constitution of this methyl ether was obtained as the result of the observation that, when oxidised by permanganate, it suffers degradation with the formation of dimethylresorcylic acid and *m*-hemipinic acid.



and

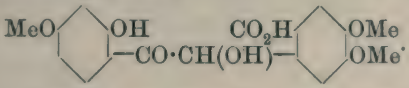


This result seems to prove conclusively that the methyl ether, $C_{18}H_{15}O_7Me$, has the constitution :

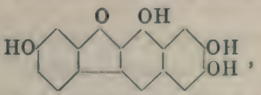


and is the *lactone* of *tetramethoxybenzoincarboxylic acid.*

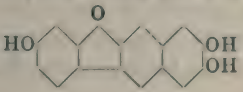
The acid, $C_{18}H_{18}O_8$, from which it was derived is therefore *hydroxytrimethoxybenzoincarboxylic acid*,



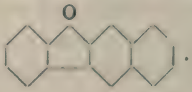
water with formation of β-anhydrotrimethylbrazilone. At the same time the methoxy-groups are attacked with formation of the tetrahydroxybrazan of the formula



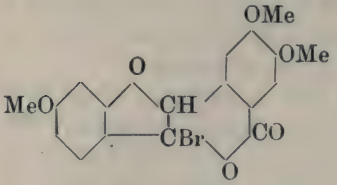
which, by the further action of the hydriodic acid and subsequently of zinc dust, is reduced to trihydroxybrazan and then to brazan :



and

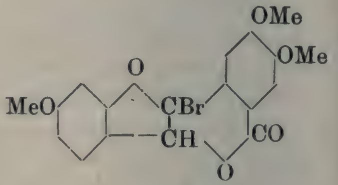


But this acid is produced by the action of alkalis on the bromolactone, $C_{18}H_{15}O_6Br$, and as the latter substance has neither acid nor phenolic properties, it seems clear that its constitution must be represented by one of the formulæ:



(I.)

or

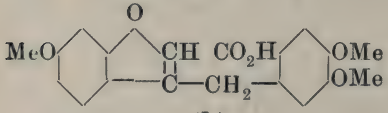


(II.)

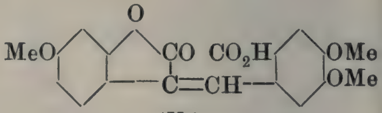
It will be observed that the skeleton structure of this bromolactone is very similar to that of ψ-trimethylbrazilone, from which it is obtained by the action of hypobromite.

We have carefully considered the probable mechanism of the formation of the bromolactone from ψ-trimethylbrazilone and potassium hypobromite, and are of the opinion that the evidence is strongly in favour of the conclusion that formula (I) represents the constitution of the bromolactone, and we therefore propose the name *trimethoxycoumarono*iso*coumarin hydrobromide* for the substance.

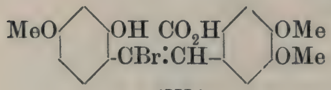
The processes involved in the formation of this substance are probably of the following nature. ψ-Trimethylbrazilone (I) is, in the first place, oxidised by the hypobromite with formation of the lactone (II). The lactone, on hydrolysis, yields the unsaturated acid, which reacts with the hypobromite with elimination of carbon dioxide and formation of the unsaturated bromo-derivative (III),



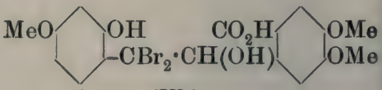
(I.)



(II.)



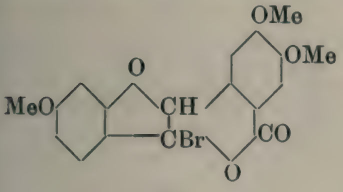
(III.)



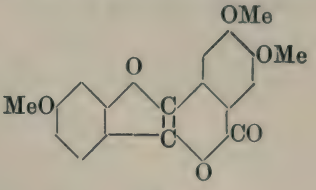
(IV.)

a process which is exactly similar to the formation of bromostyrene from cinnamic acid under the same conditions. The unsaturated bromo-derivative now unites with the elements of hypobromous acid, and the resulting dibromohydroxy-compound (IV) then loses water and hydrogen bromide and yields the bromolactone, $C_{18}H_{15}O_6Br$ (V).

It has already been mentioned that this bromolactone readily loses hydrogen bromide when it is boiled with chloroform, with formation of a lactone, $C_{18}H_{14}O_6$, and there can be no doubt that this interesting substance has the constitution (VI) and is *trimethoxycoumarono*iso-*coumarin*. Experimental evidence in confirmation of this view is described and discussed on p. 402.



(V.)

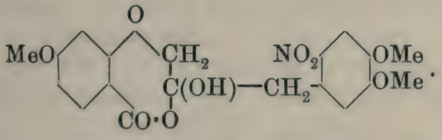


(VI.)

As far as we are able to judge, this series of investigations has produced evidence which has not only clearly demonstrated the constitutions of brazilin and hæmatoxylin, but has also afforded an explanation of each one of the remarkable series of decompositions which these substances undergo on treatment with reagents.

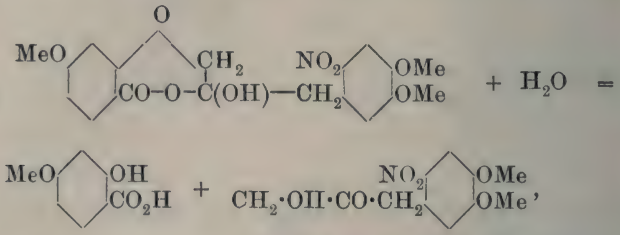
There are, however, two small exceptions to this which require discussion before this investigation is closed.

In Part VIII of this research (Trans., 1908, **93**, 500) it was shown that the remarkable substance, nitrohydroxydihydrotrimethylbrazilone, $C_{16}H_{10}O_6N(MeO)_3$, which is produced when trimethylbrazilone is treated with nitric acid, has the constitution:

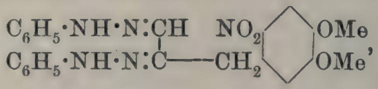


In an earlier paper (Part V, Trans., 1902, **81**, 1053) the action of phenylhydrazine on this nitro-compound was described, and it was shown that during this process the molecule is decomposed with formation of *p*-methoxysalicylic acid and a substance of the formula $C_{24}H_{25}O_4N_5$. Similar experiments on the action of phenylhydrazine on the product of the action of nitric acid on tetramethylhæmatoxylone (nitrohydroxydihydrotetramethylhæmatoxylone) yielded the same substance, $C_{24}H_{25}O_4N_5$, and an acid which was not further examined, but which was doubtless dimethoxysalicylic acid.

Careful consideration of these curious decompositions has led us to the conclusion that the correct formula for this nitrogenous substance is $C_{23}H_{23}O_4N_5$, and not $C_{24}H_{25}O_4N_5$, and the new formula agrees well with the results of analysis. In attempting to explain the mechanism of the action of phenylhydrazine in these two cases, it will only be necessary to refer in detail to its action on nitrohydroxydihydrotrimethylbrazilone. There can be little doubt that, in this decomposition, the molecule of the nitro-compound suffers scission in accordance with the scheme:



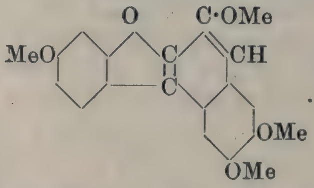
and that the latter compound then reacts with phenylhydrazine, yielding the condensation product:



a process which is very similar to the formation of glucosazone from fructose.

The other matter to which we wish to refer deals with the question of the methylation of α-anhydrotrimethylbrazilone.

Herzig (*Monatsh.*, 1902, **23**, 178) heated trimethylbrazilone with potassium hydroxide and methyl iodide, and obtained two isomeric methyl derivatives of anhydrotrimethylbrazilone, namely, a sparingly soluble substance of melting point 163—165° (α-tetramethyldehydrobrazilin), and a more readily soluble substance of melting point 130—135° (γ-tetramethyldehydrobrazilin). We have twice repeated this experiment, and in both cases obtained considerable yields of the methyl ether of melting point 163—165°, and there can be no doubt that this is methyl α-anhydrotrimethylbrazilone,



On the other hand, although we used large quantities of material in both these experiments, we obtained no evidence of the existence of a methyl ether of melting point 130—135°. During the crystallisation of the product it was noticed that a small crop of crystals was sometimes obtained which melted roughly at 130°, but, on further crystallisation, the melting point rose to 165°. We are therefore of opinion that γ-tetramethyldehydrobrazilin does not exist.

EXPERIMENTAL.

Reactions which show the similarity in Properties between α- and β-Anhydrotrimethylbrazilones and Haematoxylones and β- and α-Naphthol.

In the introduction (pp. 383, 386) it was stated that α-anhydrotrimethylbrazilone and α-anhydrotetramethylhæmatoxylone have the properties of derivatives of β-naphthol with the α-position free, and that β-anhydrotrimethylbrazilone and β-anhydrotetramethylhæmatoxylone have properties similar to derivatives of α-naphthol with the β-position free, and the constitutional formulæ given to these substances is in harmony with this view of their constitutions. The following qualitative comparison clearly brings out these points. The α-derivatives are soluble in dilute potassium hydroxide, and the β-derivatives are soluble even in cold sodium carbonate. They are all readily methylated by methyl sulphate and alkali under the same conditions as the corresponding naphthols. The azo-dyes obtained from the α-anhydro-derivatives have already been described (Trans., 1908, **93**, 500) and shown to be similar to those obtained under the same conditions with β-naphthol, and we now find that the β-anhydro-derivatives also yield colour reactions with diazo-salts which correspond very closely with those exhibited by alkaline solutions of α-naphthol. The following table will illustrate this point:

Diazotised.	β-Anhydrotrimethylbrazilone.	β-Anhydrotetramethylhæmatoxylone.
Aniline	Deep crimson	Claret.
Sulphanilic acid	Crimson (blue shade)	Purplish-red.
α-Naphthylamine	Crimson (blue shade)	Purplish-red.
Benzidine	Purple	Purple.
p-Nitroaniline	Bluish-green	Bluish-green.
m-Nitroaniline	Crimson	Crimson.
Aminoazobenzene	Olive-green	Sage-green.

A very characteristic reaction shown by both α- and β-naphthol is that their solutions in potassium hydroxide acquire a Berlin-blue colour changing to green and finally to brown, when they are mixed with chloroform and heated at 40–50° (Lustgarten, *Monatsh.*, 1882, **3**, 720). It is certainly remarkable that such complicated derivatives of the naphthols as the α- and β-anhydrotrimethylbrazilones and tetramethylhæmatoxylones should not only show this reaction, but should reproduce almost exactly the same shades of colour. In carrying out the experiment, a few drops of chloroform were added to the solution of the anhydro-derivative in alcoholic potassium hydroxide, and, on warming on the water-bath, the following behaviour was observed :

α-Anhydrotrimethylbrazilone	Berlin-blue changing to light green and then brown.
β-Anhydrotrimethylbrazilone	Bright green changing to brown.
α-Anhydrotetramethylhæmatoxylone.......	Prussian-blue changing to green and brownish-yellow.
β-Anhydrotetramethylhæmatoxylone.......	Intense Scheele-green changing to greenish-brown.

Di-α-Anhydrotrimethylbrazilone.

In order to prepare this substance, α-anhydrotrimethylbrazilone (5 grams) is dissolved in boiling methyl alcohol (200 c.c.) and digested with anhydrous ferric chloride (10 grams) on the water-bath for half an hour, when a green precipitate will have separated.

The whole is filtered hot, the precipitate washed with alcohol, and the pale green residue, which is very sparingly soluble in most organic solvents, crystallised from a large quantity of methyl ethyl ketone :

0·1219 gave 0·3138 CO_2 and 0·0495 H_2O. $C = 70·2$; $H = 4·5$.

$C_{38}H_{30}O_{10}$ requires $C = 70·6$; $H = 4·6$ per cent.

This interesting substance shrinks at 215°, and gradually melts with some decomposition to a green liquid, fusion being complete at 225°. When mixed with alcoholic sodium or potassium hydroxide, it yields sparingly soluble sodium or potassium salts ; it does not combine with diazonium salts, nor does it give any coloration with chloroform and potassium hydroxide, but sulphuric acid dissolves it with a yellowish-brown colour. In order to convert it into the derivative corresponding with β-naphthylene oxide, the substance was digested with phosphoryl chloride, the product decomposed by water, and the precipitate extracted repeatedly with dilute alcoholic potassium hydroxide. The greenish-grey residue resembles β-naphthylene oxide in a striking manner ; thus, for example, both substances dissolve in sulphuric acid, yielding a rose-red solution which, on warming, becomes successively red, violet, purple, and finally a beautiful indigo-blue.

Di-α-anhydrotrimethylbrazilone Diacetate.—This derivative is obtained when di-α-anhydrotrimethylbrazilone (2 grams) is boiled for ten minutes with acetic anhydride (20 c.c.) and anhydrous sodium acetate (3 grams). The product is poured into water, the crystalline precipitate collected, and crystallised first from methyl ethyl ketone and then from boiling acetic acid :

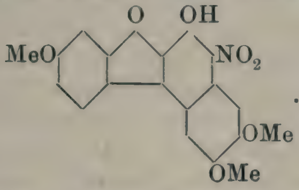
0·1236 gave 0·3117 CO_2 and 0·0532 H_2O. $C = 68·8$; $H = 4·8$.

$C_{42}H_{34}O_{12}$ requires $C = 69·0$; $H = 4·7$ per cent.

When this diacetate is slowly heated, a change is seen to occur, accompanied by slight shrinking, at about 170—175°, and there is no further change until the temperature reaches 278°, when the substance melts quite sharply. If the capillary tube containing the substance is plunged into sulphuric acid at 180°, the substance melts, but this is not the case with specimens which had previously been heated at 180° and allowed to cool. The diacetate exists evidently in two modifications, melting respectively at about 180° and at 278°.

The lower melting modification is always obtained when the substance is crystallised from acetic acid, and separates in four-sided plates, often united in the form of a cross. Its solution in methyl ethyl ketone exhibits a strong violet fluorescence.

Nitro-α-anhydrotrimethylbrazilone,



Considerable quantities of the acetyl derivative of this substance were prepared by dissolving acetyl-α-anhydrotrimethylbrazilone (Trans., 1902, **81**, 1045), in quantities of 10 grams, in warm glacial acetic acid (150 c.c.), and, after cooling, adding nitric acid (10 c.c. of D = 1·42) diluted with acetic acid (20 c.c.). The nitro-derivative crystallises almost immediately, and, after a few minutes, is collected and washed with alcohol, when a yield of 97 per cent. of that theoretically possible is obtained. For analysis, the substance was recrystallised from acetic acid:

0·1194 gave 0·2682 CO_2 and 0·0462 H_2O. C = 61·3; H = 4·3.

$C_{21}H_{17}O_8N$ requires C = 61·3; H = 4·1 per cent.

Nitroacetyl-α-anhydrotrimethylbrazilone is sparingly soluble in alcohol or cold glacial acetic acid, and separates from boiling acetic acid in small, brilliant yellow needles, which darken at 222° and melt at 235° with decomposition. It dissolves in sulphuric acid, yielding a purple solution, which becomes brown on dilution with water.

Nitro-α-anhydrotrimethylbrazilone may be obtained by the direct nitration of α-anhydrotrimethylbrazilone, but not so readily as by the hydrolysis of the acetyl derivative just described The acetyl derivative is finely powdered and digested with a large excess of very dilute methyl-alcoholic potassium hydroxide for half an hour, the red solution is then filtered from any unchanged substance and undissolved potassium salt, and the filtrate acidified with acetic acid. The crystalline precipitate is collected, washed with alcohol, and dried at 100°; it is then pure:

0·1067 gave 0·2407 CO_2 and 0·0407 H_2O. C = 61·5; H = 4·2.
$C_{19}H_{15}O_7N$ requires C = 61·8; H = 4·1 per cent.

Nitro-α-anhydrotrimethylbrazilone is very sparingly soluble even in hot glacial acetic acid, and is difficult to recrystallise.

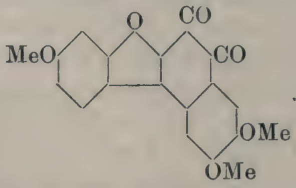
It separates from a large quantity of boiling glacial acetic acid as a brick-red powder consisting of not very well defined microscopic prisms. It dissolves in alkalis with a yellowish-red, and in sulphuric acid with a reddish-purple, colour. When digested with acetic anhydride and sodium acetate, it is converted into the acetyl derivative described above.

Nitro-α-anhydrotrimethylbrazilone Methyl Ether.—This substance is readily obtained when nitric acid (3 c.c.) is added all at once to a cold solution of α-anhydrotrimethylbrazilone methyl ether (2·5 grams: see Herzig and Pollak, *Monatsh.*, 1902, **23**, 177) in glacial acetic acid (25 c.c.). The yellow crystals, which soon separate, are collected, washed with alcohol, and crystallised from glacial acetic acid. The same substance is obtained when nitro-α-anhydrotrimethylbrazilone dissolved in boiling dilute methyl-alcoholic potassium hydroxide is treated with methyl sulphate until the red colour of the alkaline solution disappears:

0·1294 gave 4·4 c.c. N_2 at 10° and 751 mm. N = 4·0.
$C_{20}H_{17}O_7N$ requires N = 3·7 per cent.

Nitro-α-anhydrotrimethylbrazilone methyl ether separates from acetic acid in bright yellow needles, melts at 226°, and dissolves in sulphuric acid, forming a reddish-violet solution.

Trimethoxy-α-brazanquinone,



This interesting new quinone has been obtained in a variety of different ways, of which the following may be particularly mentioned.

I. *By the Oxidation of Dihydroxytrimethoxy-α-brazan.*—In carrying out this experiment, diacetoxytrimethoxybrazan (p. 396; 3 grams) was dissolved in hot alcoholic potash (30 c.c. of 3 per cent.) and a current of air passed through the solution, when a flocculent precipitate separated, which was green at first, but ultimately became brown. The precipitate was collected and crystallised from glacial acetic acid, from which the quinone separated as a brown, microcrystalline mass:

0·1105 gave 0·2726 CO_2 and 0·0437 H_2O. C = 67·3; H = 4·4.
$C_{19}H_{14}O_6$ requires C = 67·5; H = 4·2 per cent.

II. *By the Oxidation of Aminoacetyl-α-anhydrotrimethylbrazilone.*—Nitroacetyl-α-anhydrotrimethylbrazilone (p. 393; 5 grams) was suspended in boiling alcohol (500 c.c.) and reduced with zinc dust and hydrochloric acid on the water-bath until solution was complete. Water was then added, and the solution of the aminophenol oxidised by the addition of ferric chloride, chromic acid, or sodium nitrite, the latter appearing to give the best results. The well-cooled solution was mixed with sodium nitrite (2 grams), dissolved in water, and the brown precipitate, which rapidly separated, was collected, dried on porous porcelain, and crystallised from glacial acetic acid.

III. *By the Action of Potassium Hypobromite on α-Anhydrotrimethylbrazilone.*—In this experiment α-anhydrotrimethylbrazilone (2 grams) was dissolved in very dilute potassium hydroxide, mixed with powdered ice, and treated with an ice-cold solution of bromine (6 grams) in dilute potassium hydroxide. The brown precipitate of the quinone, which soon separated, was collected, and, after crystallisation from glacial acetic acid, was found to weigh 1·5 grams. The identity of the substances obtained in the above experiments was proved by careful comparison, and especially by the fact that they all yielded the same quinoxaline on treatment with 3:4-tolylenediamine, and were all converted into diacetoxytrimethoxy-α-brazan (p. 396) by treatment with zinc dust in the presence of acetic acid and acetic anhydride.

Trimethoxy-α-brazanquinone is very sparingly soluble in most solvents, and does not melt at 300°. It crystallises from much boiling acetic acid as a brown, microcrystalline powder, which consists of balls of needles. It dissolves in concentrated sulphuric acid with an intense crimson colour, and is precipitated unchanged on dilution with water.

Trimethoxy-α-brazotoluquinoxaline is obtained when the quinone (1 gram) is boiled with 3:4-tolylenediamine (1 gram), sodium acetate (1 gram), and glacial acetic acid (300 c.c.). As soon as the quinone has dissolved, the liquid is filtered and allowed to cool, when beautiful orange-brown, glistening needles separate. These are collected and recrystallised from glacial acetic acid:

0·1280 gave 0·3446 CO_2 and 0·0554 H_2O. C = 73·4; H = 4·8.
$C_{26}H_{20}O_4N_2$ requires C = 73·6; H = 4·7 per cent.

This quinoxaline melts at 257° without decomposition, and is moderately readily soluble in benzene, yielding a yellow solution which exhibits an intense green fluorescence, but the solutions in alcohol or acetic acid do not fluoresce. It is coloured crimson by concentrated hydrochloric acid, and dissolves in sulphuric acid, yielding a magnificent royal-blue solution which, when diluted with water, gives a crimson solution and then a brown precipitate.

It is mentioned above that trimethoxy-α-brazanquinone is obtained in good yield from α-anhydrotrimethylbrazilone by oxidation with potassium hypobromite. When, however, chromic acid was employed as the oxidising agent, a different result was obtained.

α-Anhydrotrimethylbrazilone (7 grams) was dissolved in glacial acetic acid, and then chromic acid (4 grams), dissolved in a little water, gradually added, the solution being constantly stirred and carefully cooled.

After a quarter of an hour, the almost black precipitate was collected, dried on porous porcelain, and crystallised from a large quantity of boiling glacial acetic acid.

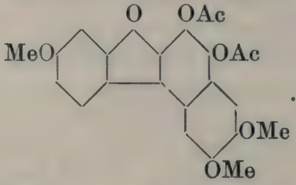
The deep green, microcrystalline mass yielded on analysis the following result:

0·1103 gave 0·2694 CO_2 and 0·0420 H_2O. C = 66·6; H = 4·2.

$C_{38}H_{30}O_{12}$ requires C = 67·2; H = 4·4 per cent.

Since this substance does not lose its green colour even after repeated crystallisation from acetic acid, it is probable that it is *trimethoxy-α-brazanquinhydrone*, a view which would be in agreement with the results of analysis.

Diacetoxytrimethoxy-α-brazan,



This interesting substance is obtained when trimethoxy-α-brazanquinone (5 grams) is boiled with acetic anhydride (20 c.c.), glacial acetic acid (50 c.c.), a trace of zinc chloride, and excess of zinc dust until the solution is colourless. The hot liquid is filtered into dilute sulphuric acid, the colourless, crystalline precipitate collected, and purified by repeated crystallisation from acetic acid:

0·1112 gave 0·2643 CO_2 and 0·0469 H_2O. C = 64·8; H = 4·7.

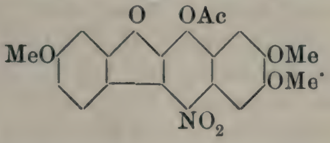
$C_{23}H_{20}O_8$ requires C = 65·1; H = 4·7 per cent.

Diacetoxytrimethoxy-α-brazan melts at 217°, and is sparingly soluble in the usual solvents. It separates from acetic acid in slender needles, from methyl ethyl ketone in bunches of microscopic threads, and from ethyl acetate or light petroleum in slender, curly threads. It is coloured green by sulphuric acid and dissolves, yielding a brown solution which becomes crimson on standing.

When its solution in acetic acid is treated with nitric acid, a yellow, crystalline nitro-derivative is produced, which darkens at 240°, melts at 310°, and dissolves with a deep purple colour in sulphuric acid.

Several attempts were made to obtain the free dihydroxy-derivative by hydrolysing the acetyl derivative under a variety of conditions, but this substance is so readily oxidised in the air that it was not found possible to isolate it in a pure condition.

Nitroacetyl-β-anhydrotrimethylbrazilone,



The acetyl-β-anhydrotrimethylbrazilone employed in this experiment was prepared by the action of sulphuric acid and then of acetic anhydride on trimethylbrazilone (Herzig, *Ber.*, 1904, **37**, 632; Herzig and Pollak, *Monatsh.*, 1904, **25**, 881). The pure acetyl derivative (5 grams) was dissolved in glacial acetic acid (100 c.c.), and the well-cooled solution gradually mixed with nitric acid (6 c.c. of D = 1·42).

After a few minutes the red solution deposited crystals of the nitro-derivative, which were collected, washed with alcohol, and crystallised from acetic acid:

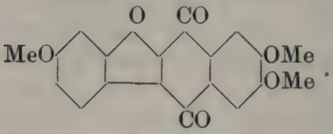
0·1316 gave 0·2945 CO_2 and 0·050 H_2O. C = 61·1; H = 4·1.

$C_{21}H_{17}O_8N$ requires C = 61·3; H = 4·1 per cent.

Nitroacetyl-β-anhydrotrimethylbrazilone is more soluble in acetic acid than the corresponding α-derivative (p. 393), and separates in microscopic, orange threads which shrink together at 246—250°.

It dissolves with a red colour in sulphuric acid. An exactly similar derivative is obtained by nitrating acetyl-β-anhydrotetramethylhæmatoxylone under the same conditions, and separates during the operation in reddish-brown needles. It is deposited from alcohol as a reddish-brown, crystalline powder, which melts at 161° with decomposition, and dissolves in sulphuric acid to an intense red solution.

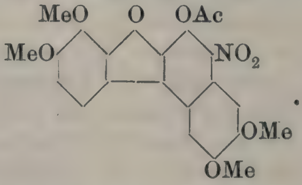
Trimethoxy-β-brazanquinone,



This interesting substance was first prepared by Kostanecki and Lloyd (*Ber.*, 1903, **36**, 2194) by the oxidation of β-anhydrotrimethylbrazilone with chromic acid (compare p. 386). We have found that it may be obtained in a very good yield from nitroacetyl-β-anhydrotrimethylbrazilone by reduction, hydrolysis, and subsequent oxidation of the amino-derivative. Nitroacetyl-β-anhydrotrimethylbrazilone (1 gram) is dissolved in boiling alcohol and treated with zinc dust and hydrochloric acid until a colourless solution is obtained. After dilution with water, the liquid is filtered and mixed with a strong aqueous solution of sodium nitrite (1 gram), when an immediate voluminous, red precipitate separates; this is collected, washed with water, and crystallised from glacial acetic acid. The small, deep red threads obtained in this way melted at 261—262°, and were found by direct comparison to be identical with the trimethoxy-β-brazanquinone prepared by Kostanecki and Lloyd. This method of preparation is interesting, not only because it is exactly analogous to the formation of trimethoxy-α-brazanquinone from α-anhydrotrimethylbrazilone (p. 394), but also because it proves conclusively that the nitro-group in nitroacetyl-β-anhydrotrimethylbrazilone occupies the position assigned to it on p. 397.

That the quinone is a para- and not an ortho-quinone is confirmed by the fact that it does not yield a condensation product with *o*-tolylenediamine.

Nitroacetyl-α-anhydrotetramethylhaematoxylone,



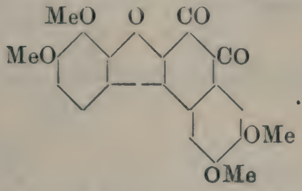
In preparing this substance, acetyl-α-anhydrotetramethylhæmatoxylone (10 grams: Trans., 1902, **81**, 1062) was dissolved in glacial acetic acid (200 c.c.) and the well-cooled solution mixed with nitric acid (15 c.c. of D = 1·42) diluted with glacial acetic acid (15 c.c.). In a short time, crystals commenced to separate, and, after two hours, the precipitate was collected and a further quantity was obtained by diluting the filtrate with water. The mass was washed with alcohol and crystallised from acetic acid :

0·1270 gave 0·2784 CO_2 and 0·0489 H_2O. $C=59·8$; $H=4·3$.

$C_{22}H_{19}O_9N$ requires $C=59·9$; $H=4·3$ per cent.

Nitroacetyl-α-anhydrotetramethylhaematoxylone separates from acetic acid in yellow needles, and melts, apparently without decomposition, at 215°. It is readily soluble in hot acetic acid or hot alcohol, but sparingly so in cold alcohol, and it dissolves in sulphuric acid, yielding an intense olive-green solution which, on dilution with water, changes to deep brown. It was mentioned on p. 393 that the solution of the corresponding brazilone derivative in sulphuric acid is purple, and it is remarkable that the introduction of a fourth methoxy-group should be sufficient to bring about so complete a change in colour.

Tetramethoxy-α-brazanquinone,



This interesting quinone was first obtained by methods similar to those described in the case of the corresponding trimethoxy-derivative (p. 394), but the most convenient method of preparation is probably the following. Nitroacetyl-α-anhydrotetramethylhæmatoxylone (1 gram) is boiled in alcoholic solution with granulated zinc and hydrochloric acid until a colourless solution is obtained, and then for ten minutes longer. The hot solution is filtered, diluted with half its volume of water, and then sodium nitrite (1 gram), dissolved in water, is added, when a brownish-black precipitate separates. This is collected, washed with cold alcohol, and crystallised from much boiling alcohol :

0·1109 gave 0·2627 CO_2 and 0·0447 H_2O. $C=64·6$; $H=4·4$.

$C_{20}H_{16}O_7$ requires $C=65·2$; $H=4·3$ per cent.

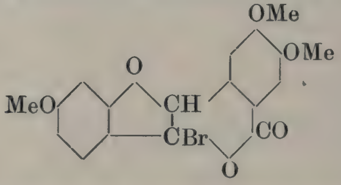
Tetramethoxy-α-brazanquinone separates from alcohol in dark brown, microscopic prisms, and is very sparingly soluble in most solvents, but moderately readily so in hot acetic acid. It dissolves in sulphuric acid, yielding a deep violet solution. When it is boiled with acetic acid, acetic anhydride, and zinc dust (compare p. 396), it is reduced and converted into a colourless acetyl derivative, which was not further examined.

Tetramethoxy-α-brazotoluquinoxaline.—This derivative is obtained when the quinone (1 gram) is digested for ten minutes with acetic acid (50 c.c.), 3:4-tolylenediamine hydrochloride (1 gram), and the same quantity of sodium acetate. The dark solution is mixed with water, the precipitate collected, washed with alcohol, and crystallised from a large quantity of toluene, from which it separates as a coffee-coloured powder consisting of microscopic needles:

0·1248 gave 0·3247 CO_2 and 0·0576 H_2O. C = 71·0; H = 5·1.
$C_{27}H_{22}O_5N_2$ requires C = 71·3; H = 4·8 per cent.

This quinoxaline shrinks at 205—210°, and is very similar in properties to trimethoxy-α-brazotoluquinoxaline described on p. 395. It dissolves in sulphuric acid with a deep indigo-blue colour, and the solution becomes pink on dilution with water. The solution of the substance in boiling toluene is brown, and, when diluted, exhibits an intense ivy-green fluorescence, and this property is so marked that, although the quinoxaline is almost insoluble in cold toluene, when it is shaken with the solvent and filtered, the almost colourless filtrate still shows a strong fluorescence.

Trimethoxycoumaronoisocoumarin Hydrobromide,



This substance is produced by the action of potassium hypobromite on ψ-trimethylbrazilone (Trans., 1908, **93**, 501), the best conditions of preparation being apparently the following.

ψ-Trimethylbrazilone (20 grams) is dissolved in potassium hydroxide (4 grams) and water (150 c.c.), and the well cooled solution poured into potassium hypobromite, made by dissolving bromine (10 c.c.) in potassium hydroxide (24 grams), water (200 c.c.), and powdered ice (200 grams). In a few seconds the new substance commences to separate, the whole liquid soon becomes gelatinous, and, after standing for four to five hours, the gelatinous mass will have become crystalline.

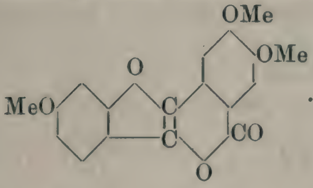
The almost colourless, very finely-divided precipitate is collected by the aid of the pump, and is best washed by rubbing in a mortar with water and again transferring to the pump, and, after repeating the operation several times, the mass is left in contact with porous porcelain until dry. Finally, the substance is dissolved in *cold* chloroform and the filtered solution precipitated by light petroleum:

0·1230 gave 0·2404 CO_2 and 0·0446 H_2O. C = 53·3; H = 4·0.
0·1460 „ 0·0634 AgBr. Br = 19·2.

$C_{18}H_{15}O_6Br$ requires C = 53·1; H = 3·7; Br = 19·6 per cent.

*Trimethoxycoumarono*iso*coumarin hydrobromide* separates from chloroform on addition of light petroleum as a precipitate which is very like flour, and under the microscope is seen to consist of prisms rather irregular in shape. It darkens somewhat at 95°, and melts at 121° to a green liquid which decomposes vigorously at about 130°; it is rather sparingly soluble in the usual organic solvents in the cold, and is unstable, since it decomposes when it is boiled with acetic acid or chloroform (see below). It dissolves in sulphuric acid with elimination of hydrogen bromide, and the pale yellow solution gradually becomes red and develops a green fluorescence.

*Trimethoxycoumarono*iso*coumarin*,



On one occasion when the action of potassium hypobromite on ψ-trimethylbrazilone was carried out apparently under the same conditions as usual (see the last section), the reaction took an abnormal course, and the product consisted entirely of yellow needles, which crystallised well from methyl alcohol and melted at 152°.

We have never been able to repeat this experiment, but we have prepared the same substance by the removal of hydrogen bromide from the hydrobromide described in the last section. This may be accomplished in many ways, but the most satisfactory is to boil the dry substance with chloroform. The hydrobromide, in quantities not larger than 0·5 gram, is digested in a test-tube with chloroform for a few minutes, and the bulk of the chloroform is then slowly distilled off, when, at a certain point in the concentration, the liquid becomes green and the solid passes into solution. As soon as the green colour is observed, the flame is removed, and the vigorous action which sets in with evolution of quantities of hydrogen bromide allowed to proceed without further heating until the green colour gives place to yellow. The product is mixed with 4 to 5 volumes of methyl alcohol, and the yellow, crystalline precipitate which separates is collected and recrystallised from methyl alcohol. Of the following analyses, the substance used in I was that which had been obtained by the direct action of potassium hypobromite on ψ-trimethylbrazilone in the experiment mentioned above. Specimens II and III were prepared by the chloroform process:

I. 0·1096 gave 0·2661 CO_2 and 0·0461 H_2O. C = 66·2; H = 4·6.
II. 0·1378 „ 0·3360 CO_2 „ 0·0595 H_2O. C = 66·5; H = 4·3.
III. 0·1226 „ 0·2965 CO_2 „ 0·0496 H_2O. C = 65·9; H = 4·5.
$C_{18}H_{14}O_6$ requires C = 66·3; H = 4·3 per cent.

All the specimens of this substance were pale yellow, and it was not found possible to remove the colour by repeated recrystallisation from methyl alcohol or other solvents. When, however, the substance was digested with weak alcoholic potash for five minutes on the water-bath, a nearly colourless solution was obtained, which remained clear after diluting with water and removal of the methyl alcohol by evaporation, and, indeed, when the solution was saturated with carbon dioxide nothing separated. Addition of hydrochloric acid precipitated a white, caseous mass, and this crystallised from methyl alcohol in beautiful needles which were now quite colourless, but in other respects the substance proved to be identical with that described above, a fact which was controlled by analysis:

0·1162 gave 0·2824 CO_2 and 0·0449 H_2O. C = 66·3; H = 4·3.

*Trimethoxycoumarono*iso*coumarin* melts at 152°, and dissolves rather readily in chloroform or acetic acid, but sparingly so in cold methyl or ethyl alcohols. It is not very soluble in boiling ethyl alcohol, and separates, on cooling, in small, colourless prisms. It dissolves in sulphuric acid, yielding a salmon-pink solution, which possesses a very intense, ivy-green fluorescence; addition of a trace of nitrite changes the colour to purple, and the fluorescence is destroyed.

That the substance is a lactone is shown by its behaviour with alcoholic potash, which has been already described. The formation of trimethoxycoumarono*iso*coumarin by the elimination of hydrogen bromide from its hydrobromide may also be brought about by boiling with acetic acid or diethylaniline, but the product obtained in these cases is not so readily purified as when prepared by the chloroform method described above.

*The Action of Bromine on Trimethoxycoumarono*iso*coumarin.*

In studying this action a dilute solution of bromine in chloroform was gradually added to the *iso*coumarin until an excess was present. The bromine was slowly absorbed with elimination of hydrogen bromide, and a quantitative experiment showed that 0·71 gram of the substance reacted with 0·39 gram of bromine, or in approximately molecular proportions. As soon as the reaction was finished, the chloroform was evaporated in a vacuum desiccator, and the solid residue several times crystallised from alcohol. The air-dried substance yielded the following results on analysis:

0·1245 gave 0·2428 CO_2 and 0·0425 H_2O. C = 53·2; H = 3·8.
0·1300 „ 0·2547 CO_2 „ 0·0484 H_2O. C = 53·4; H = 4·1.
0·1207 „ 0·0552 AgBr. Br = 19·4.
$C_{18}H_{13}O_6Br$ requires C = 53·3; H = 3·2; Br = 19·7 per cent.

*Monobromotrimethoxycoumarono*iso*coumarin* separates from alcohol as a satiny mass of yellow, prismatic plates; it melts at 206°, and decomposes at 208° with formation of a red liquid. When it is digested with alcoholic potassium hydroxide, the lactone ring is hydrolysed, but the product obtained on acidifying still contains bromine, a proof that hydrogen in an aromatic nucleus had been substituted.

On the other hand, there is strong evidence that the reaction proceeds to some extent in another direction, bromine being added to the double linking. The bromine content of the crude product which remains after evaporating the chloroform is greater than that required for substitution, and yet too low for that required for the dibromide:

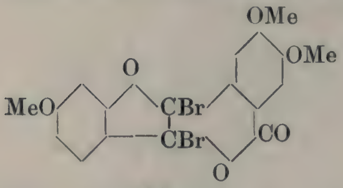
0·1114 gave 0·0643 AgBr. Br = 24·5.
$C_{18}H_{13}O_6Br$ requires Br = 19·7 per cent.
$C_{18}H_{14}O_6Br_2$ „ Br = 32·8 „ „

The presence of the dibromo-additive product seems to be borne out by the results of the following interesting experiment.

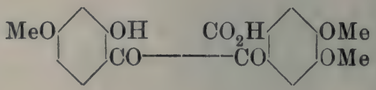
The crude product of bromination (2 grams) was dissolved in alcoholic potassium hydroxide, heated on the water-bath for half an hour, the solution diluted, evaporated until free from alcohol, cooled, and mixed with 10 c.c. of 30 per cent. hydrogen peroxide. After forty-eight hours, the solution was heated for one hour on the water-bath, acidified, filtered, saturated with ammonium sulphate, and repeatedly extracted with ether. The ethereal solution was dried, evaporated, and the solid residue, which crystallised from hot water in colourless needles, melted at 152°, and gave a violet coloration with ferric chloride, was easily recognised as *p*-methoxysalicylic acid.

The mother liquors from these crystals yielded, on concentration, an acid which was shown, by conversion into the characteristic silver salt, to be *m*-hemipinic acid.

This interesting degradation is readily explained on the assumption that the product of the bromination of trimethoxycoumarono*iso*coumarin contains the dibromo-additive compound (I), which is hydrolysed by potassium hydroxide with formation of the hydroxytrimethoxybenzilcarboxylic acid of the formula (II).



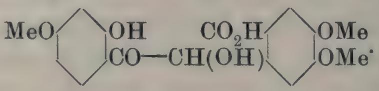
(I.)



(II.)

This acid is then oxidised by hydrogen peroxide with formation of *p*-methoxysalicylic and *m*-hemipinic acids (compare Proc., 1907, **23**, 166).

Hydroxytrimethoxybenzoincarboxylic Acid and its Lactone,



The hydroxy-acid is readily obtained by the action of alcoholic potash on trimethoxycoumaronoisocoumarin hydrobromide.

The hydrobromide (5 grams) is suspended in alcohol (100 c.c.) and warmed on the water-bath with a solution of potassium hydroxide (5 grams) in a small quantity of water, when decomposition rapidly takes place. As soon as solution is complete, the product is diluted with water, cooled, and acidified with dilute acetic acid; the gelatinous precipitate is then collected, dried on porous porcelain, and crystallised, first from methyl ethyl ketone and then from ethyl acetate:

0·1164 gave 0·2557 CO_2 and 0·0554 H_2O. C = 59·9; H = 5·3.

$C_{18}H_{18}O_8$ requires C = 59·7; H = 5·0 per cent.

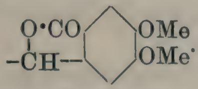
Hydroxytrimethoxybenzoincarboxylic acid melts at 195°, and is sparingly soluble even in boiling alcohol, but more readily so in ethyl acetate, from which it separates in clusters of pale yellow needles.

It is readily soluble in sodium carbonate, and dissolves in sulphuric acid, yielding a yellow solution which becomes redder on standing and develops an intense green fluorescence. Its alcoholic solution gives a brownish-violet coloration on the addition of ferric chloride.

The Lactone.—This substance was first obtained in small quantity from the product of the action of alkalis on trimethoxycoumarono*iso*coumarin hydrobromide by extraction with ether, and, on concentrating the ethereal solution, it separated as a crystalline crust (analysis I). It is best prepared from the hydroxycarboxylic acid (1 gram) by digesting with glacial acetic acid (10 c.c.) and hydrochloric acid (1 c.c.). The precipitate, obtained on dilution with water, is collected and crystallised from ethyl alcohol (analysis II):

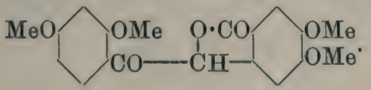
I. 0·1227 gave 0·2795 CO_2 and 0·0525 H_2O. C = 62·2 ; H = 4·8.
II. 0·1131 ,, 0·2599 CO_2 ,, 0·0498 H_2O. C = 62·7 ; H = 4·9.
$C_{18}H_{16}O_7$ requires C = 62·8 ; H = 4·6 per cent.

The *lactone* of *hydroxytrimethoxybenzoincarboxylic acid* melts at 181°, and, although sparingly soluble in alcohol, is more readily so than the hydroxy-acid. It dissolves readily in potassium hydroxide, but is insoluble in sodium carbonate. Since the alcoholic solution gives a reddish-violet coloration with ferric chloride, it is clear that the phenolic hydroxyl has not taken part in the lactone formation, and it is therefore evident that the lactone contains the grouping :



Oxidation of *Hydroxytrimethoxybenzoincarboxylic Acid.*—When this acid is heated with excess of nitric acid (D = 1·17) on the water-bath for one hour, vigorous oxidation occurs, and, on dilution with water, a sticky, yellow oil is obtained, which gives the blood-red colour with ferric chloride characteristic of nitromethoxysalicylic acid, but from which nothing crystalline could be obtained. The clear liquid from this yellow oil was extracted with ether, and yielded, on evaporation, a crystalline residue, which was recognised, by conversion into the characteristic silver salt and ethylimide (m. p. 230°), as *m*-hemipinic acid.

The Lactone of Tetramethoxybenzoincarboxylic Acid,



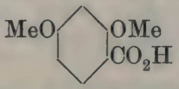
In preparing this substance, the lactone of hydroxytrimethoxybenzoincarboxylic acid (1 gram) is dissolved in the least possible quantity of methyl alcohol, mixed with methyl sulphate (10 grams), and the solution kept distinctly alkaline by the addition, from time to time, of small quantities of 40 per cent. aqueous potassium hydroxide, The vigorous action is not checked, and when the solution remains alkaline, it is diluted with water and acidified with hydrochloric acid. The chalky precipitate is collected, and crystallised first from alcohol and then from methyl ethyl ketone containing a small quantity of light petroleum :

0·1012 gave 0·2369 CO_2 and 0·0481 H_2O. C = 63·8 ; H = 5·3.
$C_{19}H_{18}O_7$ requires C = 63·7 ; H = 5·0 per cent.

The *lactone* of *tetramethoxybenzoincarboxylic acid* melts at 200°, and is moderately soluble in methyl or ethyl alcohols, acetic acid, or acetone, but almost insoluble in light petroleum. The alcoholic solution gives no coloration with ferric chloride. It dissolves in sulphuric acid, yielding a purple solution, which soon becomes carmine-red, and develops a deep green fluorescence. On long standing, the solution resembles in colour and fluorescence that of a solution of hydroxytrimethoxybenzoincarboxylic acid in sulphuric acid. The lactone is insoluble in sodium carbonate and in dilute potassium hydroxide, but it dissolves in alcoholic potassium hydroxide, and the solution remains clear on dilution with water. If the alcohol is removed by evaporation and hydrochloric acid added to the well-cooled solution, a white, amorphous substance is precipitated, which is evidently the free hydroxy-acid, since it is soluble in sodium carbonate. In a short time, however, lactone formation takes place, and the precipitate becomes insoluble.

Oxidation of Tetramethoxybenzoincarboxylic Acid.—In carrying out this oxidation, the pure lactone (15 grams) was dissolved in alcoholic potash, the solution diluted, evaporated until free from alcohol, nearly neutralised with hydrochloric acid, mixed with powdered ice, and then cold saturated permanganate added until the colour remained permanent.

After removing the slight excess of permanganate by sulphurous acid, the product was heated on the water-bath, filtered, and the yellow solution evaporated to a small bulk, acidified, and extracted several times with ether. The ethereal solution was dried over anhydrous sodium sulphate, evaporated, and the semi-solid residue dissolved in hot water, when, on standing, a crystalline acid separated which melted at 107°. That this acid was dimethyl-β-resorcylic acid,



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was proved by its properties, and especially by the fact that, when mixed with a specimen of this acid which had been obtained by the methylation of β-resorcylic acid, there was no alteration in melting point. The filtrate from the dimethyl-β-resorcylic acid was concentrated and allowed to stand, when large, prismatic crystals separated, which melted at 178° and were proved to consist of *m*-hemipinic acid by conversion into the characteristic silver salt and ethylimide (m. p. 230°).

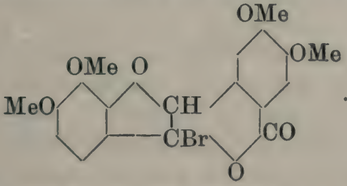
The Action of Potassium Hypobromite on ψ-Tetramethylhaematoxylone.

In studying this decomposition, ψ-tetramethylhæmatoxylone (5 grams) was dissolved in dilute potassium hydroxide and treated with a solution of bromine (3 c.c.) in dilute ice-cold potassium hydroxide, when a white precipitate soon separated, which, in appearance, closely resembled the substance obtained in the corresponding experiment with ψ-trimethylbrazilone (p. 401).

After five hours, the precipitate was collected, washed with water and alcohol, and left in contact with porous porcelain. The dry residue was extracted with boiling chloroform, and the extract mixed with alcohol, when a pink substance separated, which consisted of microscopic prisms or needles. After recrystallisation in the same manner, the substance was almost colourless:

0·1180 gave 0·2153 CO_2 and 0·0441 H_2O. C = 52·1; H = 4·2.
0·0985 ,, 0·0412 AgBr. Br = 17·8.
$C_{19}H_{17}O_7Br$ requires C = 52·2; H = 3·9; Br = 18·3 per cent.

These analytical results indicate that the substance obtained in this matter is *tetramethoxycoumaronoisocoumarin hydrobromide*,



It melts at 158° with decomposition, and, in some of its properties, differs in a rather striking manner from the corresponding trimethoxy-derivative (p. 401). Thus, for example, whilst the latter is very readily decomposed by boiling with chloroform or acetic acid with elimination of hydrogen bromide, the tetramethoxy-derivative appears to be stable towards these reagents, and is even not immediately decomposed by diethylaniline. When it is digested with potassium hydroxide, it is readily hydrolysed, with formation of an acid, free from bromine, which in alcoholic solution gives a violet coloration with ferric chloride, and in appearance and other properties resembles hydroxytrimethoxybenzoincarboxylic acid (p. 404).

The solution of the acid in potassium hydroxide was left in the cold with excess of 30 per cent. hydrogen peroxide for two days, and, after heating on the water-bath for an hour, acidified and repeatedly extracted with ether. The solid residue which remained after distilling off the ether consisted of two acids, one readily, and the other sparingly, soluble in water. The more soluble acid was recognised as *m*-hemipinic acid, and the less soluble acid, which gave an intense violet coloration with ferric chloride, was probably dimethoxysalicylic acid.

The authors wish to express their indebtedness to the Research Fund Committees of the Royal Society and Chemical Society for grants in aid of the heavy cost of this investigation.

THE UNIVERSITY,
MANCHESTER.

XLVIII.—*A Study of Some Asymmetric Compounds.*

By FREDERIC STANLEY KIPPING.

ALTHOUGH a great many externally compensated bases and acids of widely different types have been resolved into their components by fractionally crystallising their salts, and although in this way optically active compounds containing asymmetric carbon, nitrogen, sulphur, selenium, tin, and silicon atoms have been obtained, it is still impossible, even in dealing with very closely related or homologous compounds, to form any preconceived opinion as to whether a given optically active base will or will not effect the resolution of a given *dl*-acid, or a given optically active acid that of a given *dl*-base. Thus, although the *dl*-sulphonic acids derived respectively from the homologous compounds, benzylethylpropylsilicyl oxide (Kipping, Trans., 1907, **91**, 209; 1908, **93**, 457) and benzylethyl*iso*butylsilicyl oxide (Luff and Kipping, Trans., 1908, **93**, 2090), may both be resolved with the aid of methylhydrindamine, of the three homologous *dl*-bases, namely, hydrindamine, methylhydrindamine, and pheno-*α*-amino*cyclo*heptane, only the two latter are resolved by fractionally crystallising their *d*-hydrogen tartrates from water (Kipping and Hunter, Trans., 1902, **81**, 574; Tattersall, Trans., 1904, **85**, 169), in spite of the fact that hydrindamine and pheno-*α*-amino*cyclo*heptane, which contain only one asymmetric carbon atom respectively, are far more closely related to one another than to methylhydrindamine, the molecule of which contains two different asymmetric carbon atoms. Again, *dl*-hydrindamine may be resolved by crystallising its *d*-bromocamphorsulphonate from a hot mixture of ethyl acetate and alcohol (Kipping, Trans., 1903, **83**, 873), but not by crystallising its *d*-chlorocamphorsulphonate under similar conditions (Trans., 1903, **83**, 902).

Now, if the possibility of the existence in solution of definite partially racemic salts, *d*A*l*B, *d*A*d*B, or *d*A*d*B, *l*A*d*B, be excluded, it would seem that the resolution of any *dl*-compound by the method under discussion is determined entirely by the difference in solubility of the two components, *d*A*l*B and *d*A*d*B, or *d*A*d*B and *l*A*d*B, as the case may be, under the conditions chosen. If, therefore, it is known that a particular *dl*-acid, A, may be resolved by fractionally crystallising its salt with a particular optically active base, B, from a particular solvent, it might be inferred that the resolution of the *dl*-base, B, by fractionally crystallising its salt with the optically active acid, A, from the same solvent, should also be possible. Both salts contain the component *d*A*d*B, which is mixed in the first case with *l*A*d*B, in the second case with an equal quantity of *d*A*l*B; but *l*A*d*B and *d*A*l*B are enantiomorphously related, and therefore are equally soluble in any optically inactive solvent; consequently, since *d*A*d*B and *l*A*d*B are known to be separable owing to their different solubilities, it would seem that *d*A*d*B and *d*A*l*B should also be separable under the same conditions. Taking a definite example, *dl*-sulphobenzylethylpropylsilicyl oxide may be resolved with the aid of *d*-methylhydrindamine; consequently it might be concluded that *dl*-methylhydrindamine should be resolved by fractionally crystallising its salt with one of the active sulphobenzylethylpropylsilicyl oxides under the same conditions.

As such a resolution of this *dl*-base would have afforded a particularly striking demonstration of the asymmetric structure of the silicon compound just named, this case was first examined, and the salt prepared from *dl*-methylhydrindamine and one of the active silicon acids was submitted to fractional crystallisation under the same conditions as those employed in resolving the *dl*-silicon compound with the active base; the results, however, were negative, inasmuch as all fractions of the salt yielded optically inactive base. This was not due to the racemisation of the active silicon compound; when the latter was recovered from the salt, it still retained its asymmetry, and gave totally different products when treated with *d*- and with *l*-methylhydrindamine respectively.

It was thus proved that in this instance the mixture of *d*A*d*B and *d*A*l*B behaves very differently from the mixture of *d*A*d*B and *l*A*d*B.

Wishing to obtain, if possible, some other example of a similar kind, the case of tartaric acid and methylhydrindamine was examined. *dl*-Methylhydrindamine may be resolved by fractionally crystallising from water its *d*-hydrogen tartrate (Tattersall, *loc. cit.*), the *d*A*d*B salt being less soluble than the *d*A*l*B component. Experiments showed that the resolution of *dl*-tartaric acid could be accomplished, possibly even more easily than that of the base, with the aid of *d*-methylhydrindamine; by fractionally crystallising from water, both the components *l*A*d*B and *d*A*d*B may be isolated in a state of purity, and a large proportion of the *dl*-acid may be resolved.

As this result did not afford the desired confirmation of that obtained in the case of methylhydrindamine and the silicon compound, experiments were next made with mandelic acid and hydrindamine. It had been shown some years ago (Kipping and Hall, Trans., 1901, **79**, 442) that *dl*-hydrindamine is not resolved when its salt with *d*-mandelic acid is crystallised from alcohol; further, that a mixture of *dl*-hydrindamine *dl*-mandelate and *dl*-hydrindamine *d*-mandelate is not separated into different fractions when it is crystallised from alcohol; these results seemed to show that the components *d*A*d*B and *d*A*l*B had the same solubility, and, therefore, that the resolution of *dl*-mandelic acid could not be accomplished with the aid of one of the active hydrindamines.

Nevertheless, on fractionally crystallising *d*-hydrindamine *dl*-mandelate from water, the acid is resolved without the slightest difficulty; a marked difference between the several fractions both in appearance and in melting point is observed after one or two crystallisations, and the pure *l*A*d*B salt is obtained in the most sparingly soluble portions. This result was verified by repeating the experiment several times, and was confirmed by resolving the *dl*-acid with *l*-hydrindamine in a similar manner, when the pure *d*A*l*B salt was obtained as the more sparingly soluble component.

Some time having elapsed since the attempts to resolve *dl*-hydrindamine with *d*-mandelic acid were made, and ethyl alcohol (or aqueous alcohol) having then been used as solvent, it was thought advisable to repeat the experiments under conditions as nearly as possible identical with those employed in the resolution of the *dl*-acid; this was done, and the *dl*-hydrindamine *d*-mandelate was repeatedly and systematically crystallised from water, but it remained homogeneous; even when the saturated solution was seeded with the *d*A*l*B salt, not the slightest indication of a resolution was observed.

It is thus proved, by the two cases recorded above, that when a *d*A*d*B salt is mixed with an equivalent quantity of the corresponding *l*A*d*B salt in one case, and of the enantiomorphously related *d*A*l*B salt in the other, the mixtures may behave altogether differently towards a given solvent.

From this fact it must be concluded that the presence in the solution of the *d*A*d*B salt influences the solubility of the *l*A*d*B and *d*A*l*B components to a different extent.

Although up to the present there is no experimental evidence on record that the solubilities of two enantiomorphously related compounds are different when they are in presence of some other optically active substance, and attempts to obtain such evidence have failed (Kipping and Pope, this vol., p. 103), the results recorded in this paper may be interpreted in conformity with such a view; a saturated solution of *d*A*d*B + *l*A*d*B deposits *l*A*d*B, whereas a saturated solution of *d*A*d*B + *d*A*l*B deposits the partially racemic salt, even when it is seeded with *d*A*l*B.

The cause of this different effect of the *d*A*d*B salt on the enantiomorphously related *l*A*d*B and *d*A*l*B compounds may be independent of any definite combination between the molecules in the solution, or it may be due to the existence of dissolved complexes of a fixed character; that is to say, the solubility of *d*A*l*B in presence of *d*A*d*B may be greater than that of *l*A*d*B for the same reason—whatever that may be—that *d*A*l*B is more soluble in alcohol than in petroleum; on the other hand, the *d*A*d*B and *d*A*l*B components may unite to form in solution definite molecules of the partially racemic salt, possibly because the configurations of the *l*B and *d*B molecules better lend themselves to close-packing than the molecules of *d*A and *l*A.

The question as to the existence in solution of partially racemic salts has not, to the author's knowledge, been raised, although several workers have tried to find out whether or not racemic compounds exist in a dissolved state. The evidence more recently brought forward (Byk, *Zeitsch. physikal. Chem.*, 1904, **49**, 641; Ranken and Taylor, *Proc. Roy. Soc. Edin.*, 1907, **27**, 172; Stewart, Trans., 1907, **91**, 1537; Dunstan and Thole, Trans., 1908, **93**, 1815) certainly seems to point to the existence of dissolved racemic molecules; the results of this investigation indicate perhaps even more strongly the presence in solution of partially racemic molecules.

EXPERIMENTAL.

Sulphobenzylethylpropylsilicyl Oxide and Methylhydrindamine.

dl-Sulphobenzylethylpropylsilicyl oxide is easily resolved by fractionally crystallising its salt with *d*-(or with *l*-)methylhydrindamine from aqueous methyl alcohol (*loc. cit.*); the *d*A*d*B salt is ultimately obtained in a pure state in the most sparingly soluble fractions, and melts at 205—207°; the impure *l*A*d*B salt, obtained from the mother liquors, melts at about 135°, the pure compound prepared from the *l*-acid melting at 150—152°.

A sample of the sodium salt of *d*-sulphobenzylethylpropylsilicyl oxide was treated with *dl*-methylhydrindamine hydrochloride in aqueous solution; the precipitate remained oily for many hours, even when seeded with crystals of the *d*A*d*B salt, but ultimately solidified, and, after having been washed, was fractionally crystallised from aqueous methyl alcohol at the ordinary temperature; after several operations, the most sparingly soluble deposit crystallised rather more readily than the more soluble ones, and it seemed as if a resolution had occurred. After perhaps seven or eight crystallisations, the most sparingly soluble fraction, which then formed only a small proportion of the original preparation, was examined; it melted indefinitely at about 165°, and its melting point was not raised appreciably after two further crystallisations from anhydrous acetone. The salt in the more soluble fractions, which often remained oily during several days, was ultimately obtained as a lustrous, crystalline powder, free from oil, and melted fairly sharply at 150—152°.

The extreme fractions of the salt were then separately treated with a slight excess of sodium carbonate, and the methylhydrindamine was distilled in a current of steam; the distillates were neutralised with *d*-bromocamphorsulphonic acid, and the salts thus formed were fractionally crystallised from water. All the fractions of both preparations consisted of homogeneous deposits of *dl*-methylhydrindamine *d*-bromocamphorsulphonate, and not a trace of the salt of the active base could be detected. As fractional crystallisation of a mixture of *unequal* quantities of *d*- and *l*-methylhydrindamine *d*-bromocamphorsulphonates easily affords the pure salt of that active base which is present in the larger proportion (Tattersall and Kipping, Trans., 1903, **83**, 929), these results proved that the *dl*-base had not been resolved.

The sodium salt of the acid, which remained after distilling the base in steam, was examined; it gave with *l*-methylhydrindamine hydrochloride an oily precipitate which solidified only very slowly to a gelatinous mass, but with the *d*-base it gave a precipitate which crystallised immediately, and, after recrystallisation once from aqueous methyl alcohol, melted at 200—204°. Hence the acid consisted mainly, if not entirely, of the optically pure *d*-compound; that it contained a relatively very small quantity of the *l*-acid, however, seems to be probable; otherwise the observed difference in melting points of the various fractions of the *dl*-methylhydrindamine salt can hardly be accounted for.*

The fractional crystallisation of the salt obtained by combining *dl*-methylhydrindamine with a sample of the *l*-silicon derivative confirmed the above observations in every particular.

Tartaric Acid and Methylhydrindamine.

The resolution of *dl*-methylhydrindamine may be accomplished by fractionally crystallising from water its *d*-hydrogen tartrate (Tattersall, *loc. cit.*); from the most sparingly soluble fractions, the pure salt of the *d*-base is obtained, but it is not definitely stated whether or not the salt of the *l*-base can be isolated from the mother liquors.

* The possibility of the occurrence of partial racemisation during the preparation of the active silicon compounds from their methylhydrindamine salts (compare Trans. 1907 **93**, 465) has not yet been further investigated.

A sample of Kahlbaum's racemic acid (1 mol.) * was treated with *d*-methylhydrindamine (1 mol.), and the salt was fractionally crystallised from water. The first deposit, or that obtained from it after one recrystallisation, consisted almost entirely of the hydrated *d*A*d*B salt, which, when dried at 100°, melted at 151—153°, and had the same specific rotation in aqueous solution as the compound obtained in resolving the *dl*-base with the *d*-acid:

1·318 grams of anhydrous salt, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 3·48°$; whence $[\alpha]_D + 32·4°$.

After further fractionation, the intermediate portions melted indefinitely at temperatures ranging from 168° to 178°, but the most soluble ones had a much higher melting point; the latter, on recrystallisation, gave deposits of the pure anhydrous *l*A*d*B salt, identical with the compound (m. p. 197°) prepared by Tattersall by treating the *l*-base with *d*-tartaric acid; its specific rotation was determined in aqueous solution:

1·403 grams of dry salt, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 0·73°$; whence $[\alpha]_D - 6·5°$.

The pure *d*A*d*B and *l*A*d*B salts thus obtained were separately converted into the sodium salts, which were strongly dextro- and lævo-rotatory respectively.

The resolution of the *dl*-acid under the above conditions was so complete that about 4 grams of pure *d*A*d*B and about 2 grams of pure *l*A*d*B salt were obtained without any difficulty from 10 grams of the original mixture.

Mandelic Acid and Hydrindamine.

dl-Hydrindamine is not resolved when its salt with *d*-mandelic acid is fractionally crystallised from alcohol, extreme fractions obtained after many operations having the same melting point (138—140°) and the same specific rotation (*loc. cit.*).

A sample of pure *d*-mandelic acid was treated with *dl*-hydrindamine, suspended and dissolved in water, and the solution evaporated, fresh base being added from time to time until a concentrated neutral solution of the salt was obtained; on cooling, the compound separated in prisms, but when cold solutions evaporated spontaneously, hard, compact nodules were deposited. Repeated attempts were made to resolve this salt; it was fractionally crystallised from water at different temperatures, but all the deposits were similar in character, and had the same melting point (138—140°). In some experiments, the warm concentrated solution was seeded with a specimen of the *d*A*l*B component (see below), and, after a small proportion of the salt had crystallised, this was separated and re-dissolved, but the deposit still consisted of the partially racemic substance. It may be concluded, therefore, that the *dl*-base cannot be resolved with *d*-mandelic acid under such conditions.

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* This acid possibly contained a slight excess of *d*-tartaric acid, but far too small a quantity to be detected polarimetrically (Kipping and Pope, *loc. cit.*).

A sample of *dl*-mandelic acid was treated with *d*-hydrindamine (Trans., 1903, **83**, 876) as described in the case of the *d*-acid and the *dl*-base. On cooling the concentrated aqueous solution, lustrous, transparent needles were first deposited, and then small, opaque, white masses began to form; after filtering rapidly and recrystallising this first fraction from water, a salt melting at 160—162° was obtained. The mother liquors from this compound gave opaque deposits, which were systematically crystallised from water, a little *d*-base being added from time to time as the solutions became acid during evaporation; the several fractions thus obtained were totally different in appearance from the compact nodules of the homogeneous salt prepared from the *d*-acid and the *dl*-base, and consisted of very bulky masses, which almost completely hid the solution; very often the solutions first set to a translucent mass of extremely fine filaments, in which a white, opaque growth, resembling cotton wool in appearance, began to form and gradually extended. These observations seemed to point to the presence of two definite compounds in the deposits, but it was not found possible to isolate even one; some of these fractions melted from about 125° to 130°, others from 130° to 135°.

d-*Hydrindamine* l-*Mandelate and* l-*Hydrindamine* d-*Mandelate.*

The sparingly soluble salt melting at 160—162°, obtained by resolving the *dl*-acid with the *d*-base, is the *l*A*d*B compound; the enantiomorphously related *d*A*l*B salt was prepared in a similar manner by resolving the *dl*-acid with the *l*-base. These compounds separate from water in lustrous prisms, and, when pure, melt at about 164° if quickly heated; a mixture of the two salts melted at 138—140°.

Their specific rotations were determined in ethyl-alcoholic (99·8 per cent.) solution:

*l*A*d*B salt: 0·932 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha - 4{\cdot}11°$; whence $[\alpha_D] - 55°$.

dAlB salt: 0·844 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 3{\cdot}85^{\circ}$; whence $[\alpha]_D + 57^{\circ}$.*

The solutions used in these determinations were separately treated with sodium carbonate in excess, and the hydrindamine was distilled in a current of steam; the solutions of the sodium salts were then concentrated, made up to 25 c.c. with water, and examined polarimetrically in a 2-dcm. tube.

The solution from the *lAdB* salt gave $\alpha - 4{\cdot}25^{\circ}$, and that from the *dAlB* salt gave $\alpha + 4{\cdot}02^{\circ}$; calculating the specific rotation of the mandelic acid contained in the solutions, the values are $[\alpha]_D - 107^{\circ}$ and $+ 112^{\circ}$ respectively.

After evaporating again, the solutions of the sodium salts were separately treated with excess of dilute hydrochloric acid, and the precipitates of mandelic acid were recrystallised from a very little water and dried; they both melted at 130—132°, simultaneously with a specimen of *d*-mandelic acid.

These observations prove conclusively that *dl*-mandelic acid may be easily resolved with the aid of one of the active hydrindamines, in spite of the fact that *dl*-hydrindamine cannot be resolved with *d*-mandelic acid under the same conditions.

d-*Hydrindamine* d-*Mandelate.*

This salt, prepared from the *d*-acid and the *d*-base, crystallises from water in lustrous plates or flat prisms; it generally begins to sinter at about 144°, and melts at 147—148°, but sometimes it does not liquefy completely until the temperature rises to 157—158°. This behaviour is due to dimorphism; when the tube containing the salt is plunged into a bath already heated at 148°, complete fusion occurs, whereas if the liquefied sample is then allowed to solidify and again heated, but slowly, it does not melt until 157—158°.

The specific rotation of this salt in ethyl-alcoholic (99·8 per cent.) solution is practically the same as that of the *dAlB* compound, as shown by the following determinations (carried out by Mr. Barrowcliff):

0·997 gram, made up to 100 c.c. in a 2-dcm. tube, gave $\alpha + 1{\cdot}07^{\circ}$; whence $[\alpha]_D + 53{\cdot}8^{\circ}$.

0·990 gram, made up to 100 c.c. in a 2-dcm. tube, gave $\alpha + 1{\cdot}06^{\circ}$; whence $[\alpha]_D + 53{\cdot}6^{\circ}$.

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* A sample of the *dAlB* salt was prepared some years ago in this laboratory (by Mr. Barrowcliff) from the *d*-acid and the *l*-base, and its specific rotation was determined in ethyl-alcoholic solution with the following result:

0·995 gram, made up to 100 c.c. in a 2-dcm. tube, gave $\alpha + 1{\cdot}07^{\circ}$; whence $[\alpha]_D + 53{\cdot}6^{\circ}$.

The Specific Rotation of Mandelic Acid and its Salts.

The value given in the literature for the specific rotation of *d*-mandelic acid in aqueous solution varies from $[\alpha]_D + 150°$ to $160°$ (compare Kipping and Hall, *loc. cit.*); the *d*-acid used in the above experiments gave the following result:

0·51 gram, made up to 25 c.c. in a 2-dcm. tube, gave $\alpha + 6·36°$; whence $[\alpha]_D + 156°$.

As the specific rotations of the *l*- and *d*-acids, calculated from the results obtained with solutions of their sodium salts, were only $[\alpha]_D - 107°$ and $+112°$ respectively, and as these sodium salts were doubtless optically pure, it was obvious that the molecular rotation of the sodium salt must be very much smaller than that of the free optically active acid.

This conclusion was confirmed; the solution of *d*-mandelic acid which gave $\alpha + 6·36°$, $[\alpha]_D + 156°$, was treated with about 0·6 gram of hydrated sodium carbonate, concentrated a little, and again made up to 25 c.c. and examined in a 2-dcm. tube; the result was $\alpha + 4·82°$; whence the specific rotation calculated for the free *acid* is $[\alpha]_D + 118°$. The difference between this value and those ($-107°$ and $+112°$) given above is probably due to a difference in the quantities of sodium carbonate present in the solutions.

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XLIX.—*The Action of Ethylene Dibromide on Monomethylaniline.*

By JOHN GUNNING MOORE DUNLOP and HUMPHREY OWEN JONES.

THE action of ethylene dibromide on monomethylaniline was investigated by one of us in 1906, in order to prepare diphenyldimethylethylenediamine, $NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh$, with the view of examining compounds containing two asymmetric nitrogen atoms.

A mixture of the two in the proportion of one gram-molecule of ethylene dibromide to two gram-molecules of monomethylaniline was heated on a water-bath under a reflux condenser for several days. The viscous mass thus obtained was treated with potassium hydroxide, and the oil which separated was dried and distilled under diminished pressure.

An oil which distilled at about 100°/12 mm. appeared to be monomethylaniline, then at 230—235° a solid distilled, which, when crystallised from alcohol, ether or light petroleum, separated in lustrous plates melting at 163°:

0·1800 gave 0·5295 CO_2 and 0·1285 H_2O. C = 80·2; H = 7·93.
0·1533 „ 16·3 c.c. N_2 at 18° and 736 mm. N = 12·0.
$C_{16}H_{20}N_2$ requires C = 80·0; H = 8·33; N = 11·7 per cent.

Molecular-weight determinations by the cryoscopic method in benzene gave results in sufficiently close agreement with the expected value, 240.

The compound did not appear to be well suited to the purpose in hand, and in February, 1907, a paper by Fröhlich appeared (*Ber.*, 1907, **40**, 763), in which a compound prepared by the action of four gram-molecules of monomethylaniline on one of ethylene dibromide at 60—70°, was described as "NN′-dimethyläthylendianilin." This base crystallised in prisms melting at 47°, and on analysis gave:

C = 79·77; H = 8·58; C = 79·80; H = 8·49; N = 11·56, 11·76,

results also satisfactory for the supposed compound.

Previous to this (*Ber.*, 1898, **31**, 3256), Bischoff stated that he had obtained a compound by the action of ethylene dibromide on monomethylaniline (proportions not given) which crystallised in plates melting at 165°. In Fröhlich's paper this discrepancy is dismissed in a footnote to the effect that it was an error.*

The subject seemed worthy of further investigation, but the pressure of other work prevented this until recently.

On examining the reaction between ethylene dibromide and monomethylaniline in different proportions at different temperatures, it was found that up to 100° the result was independent of the temperature, and depended only on the relative proportions of the two substances present.

When two gram-molecules of monomethylaniline and one of ethylene dibromide were used, the compound melting at 163° was always obtained, but the yield was in every case poor (50 grams of monomethylaniline gave only about 5 grams of the pure compound).

When five gram-molecules of base to one of ethylene dibromide were taken, the prisms described by Fröhlich as melting at 47° were produced, and the yield was fairly good (35 grams of base yielded about 10 grams of the pure compound).

---

* (*Loc. cit.*) "Vergl. diese Berichte **31**, 3256 (1898). Die Angabe eines Schmp. 165° muss auf einem Irrtum beruhen."

The method of preparation used in both cases was the same as that described above, but in the later work the vacuum distillation was omitted. The bases liberated by alkali were distilled until a temperature of about 200° was reached, and the residue was extracted with alcohol or light petroleum The compounds separated from these solutions on keeping. At least four days' heating under a reflux condenser on a water-bath is advisable if a good yield is desired.

Molecular-weight determinations in benzene solution by the cryoscopic method gave the following results:

Compound, m. p. 47°:

0·2012, in 20·96 benzene, gave $\Delta t = -0·214$. M.W. = 236.

Compound, m. p. 163°:

0·3535, in 17·69 benzene, gave $\Delta t = -0·440$. M.W. = 237.

$NMePh\cdot CH_2\cdot CH_2\cdot NMePh$ requires M.W. = 240.

Nothing therefore which had hitherto been done could give any clue to the nature of the difference between the compounds.

Properties of the substance melting at 47°.—Crystalline needles, fairly soluble in alcohol, ether, light petroleum, or benzene. The base is very soluble in hydrochloric acid, from which needles of a hydrochloride could be crystallised with some difficulty. Gravimetric synthesis and analysis of this gave results corresponding with a dihydrochloride:

0·5011 gave 0·6626 hydrochloride. Ratio, hydrochloride/substance = 1·32 : 1.

0·4183 gave 0·3665 AgCl. Cl = 21·7.

The monohydrochloride requires above ratio = 1·15 : 1. Cl = 12·8 per cent.

The dihydrochloride requires above ratio = 1·30 : 1. Cl = 22·6 per cent.

(It was found to be difficult to purify this compound, owing to its great solubility.)

The solution of the base in hydrochloric acid gives, with platinic chloride, a precipitate of very small, orange needles, which decompose on heating.

The base combines with methyl iodide in the cold to give a crystalline compound fairly soluble in alcohol, from which it separates in prisms melting at 163°:

0·1712 required 9·05 c.c. $N/20$-$AgNO_3$. I = 33·6.

$NMePh\cdot CH_2\cdot CH_2\cdot NMePh,MeI$ requires I = 33·2 per cent.

On heating the base with methyl iodide in a sealed tube at 100°, the resulting compound was practically insoluble in alcohol, and separated from hot water in prisms melting at 219°:

0·1537 required 11·65 c.c. $N/20$-$AgNO_3$. I = 48·3.

$NMePh\cdot CH_2\cdot CH_2\cdot NMePh,2MeI$ requires I = 48·46 per cent.

The compound melting at 47° was heated in a current of dry hydrogen chloride to 205—210°, when methyl chloride was evolved and a solid residue obtained, which, when extracted with water and treated with sodium hydroxide, yielded a crystalline precipitate soluble in alcohol and ether; after recrystallisation this melted at 65°, and corresponded in every respect with diphenylethylenediamine,

$$NHPh\cdot CH_2\cdot CH_2\cdot NHPh,$$

prepared by Hofmann (*Proc. Roy. Soc.*, 1859, **9**, 388; compare also Morley, *Ber.*, 1879, **12**, 1794, and Bischoff, *Ber.*, 1889, **22**, 1783). It therefore appears that the compound melting at 47°, resulting from the action of methylaniline (4 mols.) on ethylene dibromide (2 mols.), is diphenyldimethylethylenediamine, $NMePh\cdot CH_2\cdot CH_2\cdot NMePh$.

This was confirmed by preparing the compound melting at 47° from diphenylethylenediamine by the action of methyl iodide at 100°.

It still remains to determine the constitution and mode of formation of the compound melting at 163°.

Properties of the compound melting at 163°.—The compound is sparingly soluble in all solvents, being very much less soluble than the compound melting at 47°. It is sparingly soluble in hydrochloric acid on boiling, and from the solution short, lustrous prisms of the hydrochloride readily separate on cooling:

0·5052 gave 0·6641 hydrochloride. Ratio, hydrochloride/substance = 1·31 : 1.

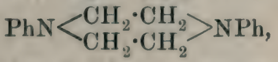
0·3478 gave 0·3242 AgCl. Cl = 23·0.

A platinichloride was obtained as a fine brown, crystalline precipitate.

With methyl iodide the same product was obtained either at the ordinary temperature (analysis I) or at 100° (analysis II); this was fairly soluble in alcohol, from which it separated in plates melting at 183°:

I. 0·2744 gave 0·1680 AgI. I = 33·1.
II. 0·1821 „ 0·1113 AgI. I = 33·1.

It appeared on consideration that the properties of this substance closely resembled those of diphenylpiperazine,



$$PhN{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}NPh,$$

prepared by Hofmann (*loc. cit.*) by the action of excess of ethylene dibromide on aniline. We therefore prepared diphenylpiperazine in this way, and found it to be identical in all respects with the compound melting at 163°, and obtained from monomethylaniline. The melting points of the two compounds and that of a mixture of the two in any proportions were identical. The analytical results previously obtained (pp. 417, 418):

$$C = 80·2;\ H = 7·93;\ N = 12·0;\ M.W. = 237$$

are in close agreement with those required by $C_{16}H_{18}N_2$, namely, C = 80.7 ; H = 7·63 ; N = 11·8 per cent. M.W. = 238.

The dihydrochloride requires Cl = 22·8 per cent. (Found, Cl = 23·0), and the methyl iodide compound requires I = 33·4 per cent. (Found, I = 33·1). Another analysis gave the following result :

0·2510 gave 0·7390 CO_2 and 0·1710 H_2O. C = 80·3 ; H = 7·57.

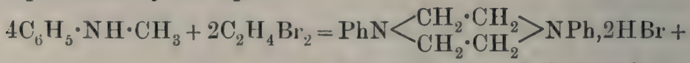
Since the compositions of diphenylpiperazine and diphenyldimethylethylenediamine differ only by two atoms of hydrogen, in such large molecules analytical results do not distinguish between them effectively.

The formation of diphenylpiperazine from monomethylaniline and ethylene dibromide would involve the elimination of the methyl groups from the former probably as methyl bromide. If methyl bromide could actually be detected among the products of the reaction, the mechanism of the process would be clear. However, there is present in the mixture a secondary base, methylaniline, which would probably react immediately with methyl bromide, giving a tertiary base. If, therefore, we could detect dimethylaniline in the oil distilling between 180° and 210°/760 mm., it would be very probable that methyl bromide had been removed from one molecule of methylaniline and had reacted with another molecule of the same base.

It was actually found that the oil boiling at about 190° consisted almost entirely of dimethylaniline, as proved by the preparation from it of nitrosodimethylaniline, by its reaction with methyl iodide, and by the absence of any action with acetyl chloride.

It was then shown that the methyl bromide was removed by direct interaction of ethylene dibromide and diphenyldimethylethylenediamine (m. p. 47°), since diphenylpiperazine was obtained when these were heated together at 100° for some days.

The above facts show that the reaction between two molecules of monomethylaniline and one of ethylene dibromide is to be represented by the equation :



$$4C_6H_5{\cdot}NH{\cdot}CH_3 + 2C_2H_4Br_2 = PhN\left<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\right>NPh,2HBr +$$

Diphenylpiperazine hydrobromide.

$$2C_6H_5{\cdot}N(CH_3)_2\,HBr$$

Dimethylaniline hydrobromide.

and is to be added to the number of abnormal reactions which have been observed to take place between alkylhalides and secondary and tertiary bases. This reaction, however, differs from other abnormal reactions in that a methyl group is actually displaced, whereas in other cases it is the methyl group which has been found to displace other alkyl groups.

Summary.

It has been shown that by the interaction of four gram-molecules of monomethylaniline and one of ethylene dibromide, diphenyldimethylethylenediamine, $\mathrm{NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh}$, and monomethylaniline hydrobromide are formed, whereas by the interaction of two gram-molecules of monomethylaniline with one of ethylene dibromide, diphenylpiperazine and dimethylaniline hydrobromide are formed.

The hydrochlorides of both bases and the quaternary compounds formed by both bases with methyl iodide are described.

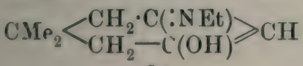
The expenses of this investigation have been defrayed by a grant from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

University Chemical Laboratory,
Cambridge.

L.—*The Condensation of Dimethyldihydroresorcin with Ethylamine.*

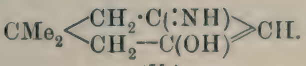
By Paul Haas.

During the course of another investigation, which is not yet completed, several unsuccessful attempts were made to prepare the ethyl derivative (I) of 5-imino-3-hydroxy-1 : 1-dimethyl-Δ^3-*cyclo*hexene (II) by acting on the latter with ethyl iodide.



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{\cdot}C(:NEt)}\\ \mathrm{CH_2{-}C(OH)}\end{matrix}>\mathrm{CH}$$

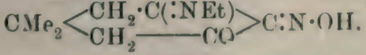
(I.)



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{\cdot}C(:NH)}\\ \mathrm{CH_2{-}C(OH)}\end{matrix}>\mathrm{CH.}$$

(II.)

It was found, however, that the compound (I) could be readily obtained by the condensation of dimethyldihydroresorcin with ethylamine. The somewhat striking colour change which is produced when the compound (I) is acted on by nitrous acid has led to the description of this substance and its reactions in a separate communication. When suspended in water and treated with nitrous acid, it is converted into a bright carmine-coloured iso*nitroso*-derivative (III), which crystallises with two molecules of water.



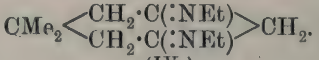
$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2{\cdot}C(:NEt)}\\ \mathrm{CH_2{-}{-}{-}CO}\end{matrix}>\mathrm{C{:}N{\cdot}OH.}$$

(III.)

The anhydrous substance obtained by drying the above carmine crystals in a vacuum is dark blue.

On treatment with potassium hydroxide, this substance loses ethylamine, and is converted into the potassium salt of *iso*nitrosodimethyldihydroresorcin (Trans., 1907, **91**, 1438). Similarly, when reduced with tin and hydrochloric acid, it loses ethylamine, and is converted into aminodimethyldihydroresorcin (*loc. cit.*, 1443).

With the object of ascertaining what effect the introduction of a second ethylamine complex would have on the colour of the *iso*nitroso-derivative, the *diethylimino*-derivative (IV) was prepared by condensing ethylamine with chlorodimethyl*cyclo*hexenone.



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot C(\colon NEt)}\\ \mathrm{CH_2\cdot C(\colon NEt)}\end{matrix}>\mathrm{CH_2}.$$

(IV.)

When treated with nitrous acid, however, the substance loses one of its ethylimino-groups, and yields the same *iso*nitroso-derivative (III) as was obtained from the monoethylimino-derivative (I).

EXPERIMENTAL.

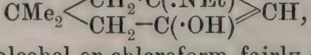
Action of Ethylamine on Dimethyldihydroresorcin.

Twenty grams of dimethyldihydroresorcin dissolved in 25 grams of alcohol and 24 grams of a 33 per cent. alcoholic solution of ethylamine were heated in a flask connected with a reflux condenser for five hours over a water-bath. The alcohol and excess of ethylamine were then distilled off, and the residue, after drying in a vacuum, was recrystallised from acetone; yield about 19 grams. The air-dried substance gave on analysis the following numbers:

0·1188 gave 8·6 c.c. N_2 (moist) at 8° and 778 mm. N = 8·94.

$C_{10}H_{17}ON$ requires N = 8·38 per cent.

3-*Hydroxy*-5-*ethylimino*-1 : 1-*dimethyl*-Δ^3-cyclo*hexene*,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot C(\colon NEt)}\\ \mathrm{CH_2{-}C(\cdot OH)}\end{matrix}\geqslant\mathrm{CH},$$

is readily soluble in alcohol or chloroform, fairly so in acetone, benzene or hot water, sparingly soluble in ether, and insoluble in light petroleum. It crystallises from a mixture of acetone and light petroleum in transparent, oblong plates, and melts at 118—120°. In alcoholic solution the substance gives a brownish-red colour with ferric chloride.

The *hydrochloride*, $C_{10}H_{17}ON,HCl$, obtained by evaporating the base with dilute hydrochloric acid, crystallises from a mixture of alcohol and ether in colourless, glistening prisms; it softens at 166°, and melts at 168—170°:

0·3378 requires 16·3 c.c. *N*/10-KOH = 0·0596 HCl. HCl = 17·63.

$C_{10}H_{17}ON,HCl$ requires HCl = 17·93 per cent.

The *platinichloride*, $(C_{10}H_{17}ON)_2,H_2PtCl_6$, was prepared by mixing alcoholic solutions of the base and platinic chloride. On adding ether, the salt was precipitated in yellow, four-sided plates; it melts at 185—186°:

0·3016 gave 0·0783 Pt. Pt = 26·12.

$C_{20}H_{36}O_2N_2Cl_6Pt$ requires Pt = 26·21 per cent.

*Action of Nitrous Acid on Hydroxyethyliminodimethyl*cyclo*hexene.*

Two grams of the finely-powdered ethylimino-compound were suspended in a well-cooled solution of 1·5 grams of potassium nitrite in 15 c.c. of water. On the addition of a drop of dilute hydrochloric acid, a very bright carmine colour was produced; the addition of acid was continued until the solution gave a reaction with starch-potassium iodide paper; the white suspended solid had now been replaced by a carmine-coloured, crystalline precipitate, which, after filtering and washing with a little water and drying, weighed 2·3 grams. The substance was recrystallised from water, and the air-dried crystals gave the following numbers on analysis:

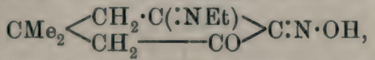
0·1376 gave 0·2588 CO_2 and 0·1112 H_2O. C = 51·25; H = 8·97.
0·1538 „ 16·1 c.c. N_2 (moist) at 11° and 762 mm. N = 12·52.
$C_{10}H_{16}O_2N_2,2H_2O$ requires C = 51·72; H = 8·62; N = 12·07 per cent.

When dried in a vacuum, the crystals become anhydrous, and turn blue; analysis of the blue solid gave the following numbers:

0·1332 gave 0·2972 CO_2 and 0·0982 H_2O. C = 60·85; H = 8·19.

$C_{10}H_{16}O_2N_2$ requires C = 61·22; H = 8·16 per cent.

4-*Oximino*-5-*ethylimino*-1 : 1-*dimethyl*cyclo*hexan*-3-*one*,



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot C(:NEt)}\\ \mathrm{CH_2{-}{-}{-}{-}CO}\end{matrix}>\mathrm{C:N\cdot OH},$$

crystallises from water with two molecules of the solvent in long, carmine-coloured, prismatic plates, which melt with decomposition at 152—153°; when dried in a vacuum, the crystals lose two molecules of water, which they again absorb on exposure to the air:

0·1304, on exposure to the air, gained 0·0234. H_2O = 15·21.

$C_{10}H_{16}O_2N_2,2H_2O$ requires H_2O = 15·52 per cent.

The hydrated substance is fairly soluble in cold, and readily so in hot, water; it dissolves readily in cold alcohol, acetone, chloroform, or ethyl acetate, yielding a blue solution, and dissolves in benzene to a red solution. An aqueous solution of the substance is neutral to litmus, and gives a deep azure-blue colour with ferrous sulphate.

Action of Potassium Hydroxide.—When treated with a warm 20 per cent. solution of potassium hydroxide, the carmine crystals dissolve to a brown solution, which gradually becomes blue and evolves ethylamine; the solution contains the potassium salt of *iso*nitrosodimethyldihydroresorcin (Trans., 1907, **91**, 1438).

Reduction with Tin and Hydrochloric Acid.—Five grams of the carmine crystals were finely powdered and dissolved in 12 grams of concentrated hydrochloric acid; 12 grams of granulated tin were then introduced in portions, and a further quantity of 6 grams of acid were added. After twelve hours the mixture was largely diluted with boiling water and saturated with hydrogen sulphide. On filtering off the stannous sulphide, the solution was evaporated to a small bulk, cooled with ice, and treated with potassium nitrite until it reacted with starch-potassium iodide paper. On extracting the solution with ether, a small quantity of a crystalline solid was obtained, which proved to be identical with the substance, "A," originally obtained by the reduction of *iso*nitrosodimethyldihydroresorcin (*loc. cit.*, p. 1441).

*Action of Ethylamine on Chlorodimethyl*cyclo*hexenone.*

Ten grams of chlorodimethyl*cyclo*hexenone were heated with 28 grams of a 33 per cent. alcoholic solution of ethylamine for three hours at 100°. The resulting brown liquid was then evaporated over a water-bath, when a brown syrup was obtained, which, after remaining for some time in a vacuum desiccator, gradually solidified. On exposure to the air, this substance at once became liquid; it was very soluble in water or alcohol, but insoluble in most other organic solvents. As it could not be obtained in a condition pure enough for analysis, it was converted into its *platinichloride*; this substance, which was precipitated from an alcoholic solution in yellow, hexagonal plates, melts and decomposes at 208°:

0·3064 gave 0·0750 Pt. Pt = 24·47.

$(C_{12}H_{22}N_2)_2,H_2PtCl_6$ requires Pt = 24·43 per cent.

Action of Nitrous Acid.—One gram of the above condensation product dissolved in an aqueous solution of potassium nitrite, on treatment with dilute hydrochloric acid, yielded 0·4 gram of carmine crystals, which proved to be the *iso*nitroso-derivative of the monoethylimino-compound described on page 423.

In conclusion, the author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the cost of this investigation.

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London, S.E.

LI.—*An Interpretation of the Hantzsch-Werner Hypothesis.*

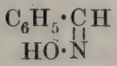
By Martin Onslow Forster and Frederick Percy Dunn.

The examination of a difference in behaviour displayed by the two *iso*nitrosocamphors towards diazomethane (Forster and Holmes, Trans., 1908, **93**, 242) has led us to extend the inquiry to several typical oximes in the hope of throwing fresh light on the constitution of these remarkable substances. Experiments have been conducted with five pairs of aldoximes, namely, benzaldoxime itself, the three nitrobenzaldoximes, and *p*-triazobenzaldoxime, with the uniform result that the *anti*aldoximes alone have been found to yield their respective *O*-methyl ethers. Of the *syn*aldoximes examined, all escape attack excepting the *m*-nitrobenz*syn*aldoxime, which has the extraordinary property of undergoing transformation into the *O*-methyl ether of the *anti*aldoxime, the quantity of this ether generated in the action being about five times that produced from the *anti*aldoxime itself. In the following summary of the results obtained under conditions to be described, the percentages must be regarded as approximations only.

	Anti.	*Syn.*
Benzaldoxime	Over 50 per cent. of ether..	Unchanged.
o-Nitrobenzaldoxime	6 per cent. of ether	,,
m-Nitrobenzaldoxime	6 ,, ,, ...	30 per cent. of *anti*-ether.
p-Nitrobenzaldoxime	37 ,, ,, ...	Unchanged.
p-Triazobenzaldoxime	50 ,, ,, ...	,,

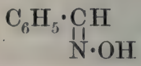
Camphoroxime and benzophenoneoxime escape attack, whilst the benzilmonoximes are transformed into oily products, as to which we do not feel justified in making a positive statement, although there is evidence that the *α*-oxime yields a *N*-methyl ether not produced from the isomeride. The oximes previously examined are the *iso*nitrosocamphors, of which the unstable modification is transformed into the stable one, this in turn yielding the *N*-methyl ether (*loc. cit.*), and quinoneoxime (von Pechmann and Seel, *Ber.*, 1898, **31**, 296), which gives rise to the *O*-methyl ether in association with glyoxime *N*-bishydroxyphenyl ether.

Surveying this experimental material, we cannot claim that it renders the oxime problem any the less perplexing. The principal outcome of the investigation is to emphasise the untrustworthy character of diazomethane as an exploring agent for the hydroxyl group. This has been brought recently into prominence by Schlotterbeck (*Ber.*, 1907, **40**, 479), who transformed aldehydes into ketones by diazomethane (compare also H. Meyer, *ibid.*, 847), and was already suggested by the production of pyrazoline from ethylene, and of pyrazolinedicarboxylic ester from fumaric ester, under the influence of the agent in question. Until this point was appreciated, we were disposed to regard the immunity of the *syn*aldoximes in a light unfavourable to the presence of a hydroxyl group, and consequently as inimical to the stereochemical hypothesis, and even now the alternative supposition is not easy to accept, since the operation of steric hindrance or steric furtherance might be expected to select the latter of the configurations:



$$\begin{array}{r} C_6H_5\cdot CH \\ \| \\ HO\cdot N \end{array}$$

Benz*anti*aldoxime.



$$\begin{array}{l} C_6H_5\cdot CH \\ \quad\;\; \| \\ \quad\;\; N\cdot OH \end{array}$$

Benz*syn*aldoxime.

for attack by an adding agent.

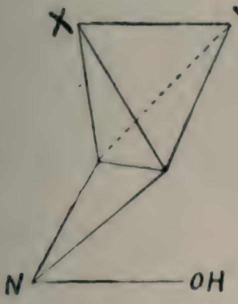
The reasons underlying the wide acceptance of the Hantzsch-Werner hypothesis are to be found, primarily, in the remarkable facility with which the two forms are interconvertible, and with respect to this we have found that the nitrobenz*syn*aldoximes are transformed into the respective *anti*-modifications by solvents even more smoothly than has been realised hitherto, so that the recorded melting points are in each case too low, doubtless because the crystals were not removed from the mother liquor without delay.

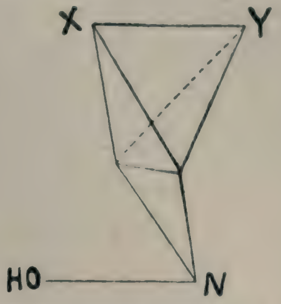
Syn.	Recorded m. p.	M. p. (F. and D.).
o-Nitrobenzaldoxime	136°	154°
m-Nitrobenzaldoxime	116—118	123
p-Nitrobenzaldoxime	176	182—184

Incidentally, this removes one of the exceptions (*m*-nitrobenzaldoxime) to the generalisation that the *syn*aldoxime melts higher than the isomeride.

A more convincing argument for the stereochemical hypothesis depends on the fact that many pairs of *O*-ethers exist, of which the *syn*-forms are readily convertible into the isomerides. Furthermore, the absence of any appreciable spectrochemical divergence between the two benzaldoximes (Hartley and Dobbie, 1900, **77**, 509) is hard to reconcile with structural difference.

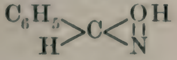
The principal obstacle to embracing the stereochemical hypothesis lies in the difficulty of giving any definite physical interpretation to the paper distinction between the two forms. The assumption underlying the hypothesis is the distribution of the valency directions of tervalent nitrogen along the edges of a tetrahedron at an apex of which the nitrogen atom is supposed to lie, and critics of the hypothesis very pertinently inquire how such an arrangement can attain to the rigidity demanded by the permanent existence of separate entities related in the manner shown by the figures:



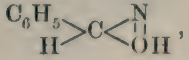


The mutual independence of these two configurations is referred by Hantzsch and Werner to the attraction exerted for one another by *Y* and *OH* in one form, *X* and *OH* in the other, so that a compound in which *X* and *Y* are identical, or one in which the attraction of *X* for *OH* far exceeds that of *Y* for *H*, would occur in one form only. Similar reasoning is adopted by Pickering (Trans., 1893, **63**, 1069) in his criticism of the Hantzsch-Werner hypothesis.

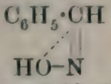
There is one factor in the problem, however, which we believe has been overlooked, namely, the possibility of some attractive force exerted between the azethenoid carbon and the hydroxylic oxygen. It is significant that among the six types of condensed ammonia derivatives, $X\cdot CH{:}N\cdot OH$, $X\cdot CY{:}NOH$, $X\cdot CY{:}N\cdot NHZ$, $X\cdot CY{:}N\cdot NH\cdot CO\cdot NH_2$, $X\cdot CH{:}NY$, and $X\cdot N{:}NY$, isomerism has been established with certainty in connexion with the first four only, and that these are the types in which the atom directly associated with azethenoid nitrogen on the side remote from the double linking is possessed of supplemental valency. Without going so far as to regard the oxygen as quadrivalent:



$$\begin{array}{l}C_6H_5\\H\end{array}\!>C<\!\begin{array}{l}OH\\ \vdots\\ N\end{array} \qquad \begin{array}{l}C_6H_5\\H\end{array}\!>C<\!\begin{array}{l}N\\ \vdots\\ OH\end{array},$$

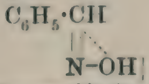


for which we are not aware that any evidence exists, we think it may well happen that the partial valency of the azethenoid carbon, affecting the dormant supplemental valency of the hydroxylic oxygen, sets up the systems:



$$\begin{array}{c}C_6H_5\cdot CH\\ \diagup\;\|\\ HO-N\end{array}$$

Benz*anti*aldoxime.

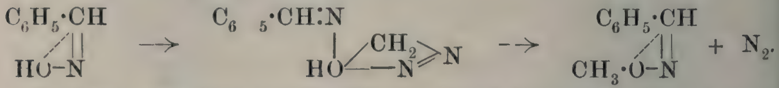


$$\begin{array}{c}C_6H_5\cdot CH\\ \|\;\diagdown\\ N-OH\end{array}$$

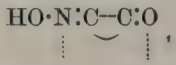
Benz*syn*aldoxime.

in which the carbon is not firmly combined with the oxygen, but associated, with sufficient intimacy to set up the directional bias indispensable to isomerism. Whether the partial valency of the nitrogen undergoes corresponding satisfaction would not affect the situation materially.

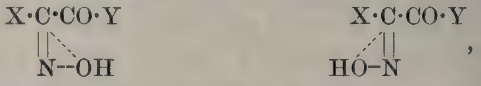
This suggestion, although failing to explain the immunity from attack displayed by the *syn*aldoximes, would at least account for the production of *O*-ethers instead of *N*-ethers from the *anti*-modifications, since the complex $-CH_2\cdot N\colon N-$ might be expected to dissolve the carbon-oxygen association, and in so doing become attached to the oxygen, and forthwith lose nitrogen, when the attraction between azethenoid carbon and hydroxylic oxygen would once more assert itself, producing an *O*-methyl ether capable of existing in two stereochemical forms:



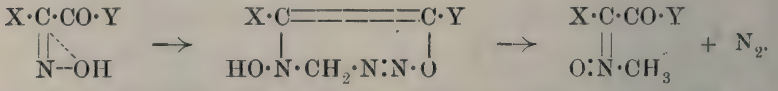
Slightly different considerations would apply to the benzilmonoximes and the *iso*nitrosocamphors. Ignoring for a moment the suggested association between azethenoid carbon and hydroxylic oxygen, these compounds would contain a conjugated linking:

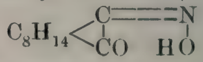


and on adding the elements of diazomethane, these would form a circuit with nitrogen and oxygen leading to a *N*-methyl ether; but according to the proposal made in this paper the *iso*nitrosoketones would have the configurations:

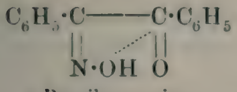


from which the conjugated linking is absent. This, however, might be developed when the diazomethane proceeded to dissolve the carbon-oxygen association, and in the resulting turmoil of conflicting affinities could secure for itself the adding agent, forming therewith a *N*-methyl ether:

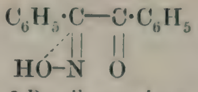


Even regarding the behaviour of *α*-benzilmonoxime as doubtful, it has been established that the stable *iso*nitrosocamphor yields the *N*-methyl ether, and for reasons already detailed (Forster, Trans., 1905, **87**, 232), the configuration  $C_8H_{14}<\begin{matrix}C{=\!=\!=}N\\ |\qquad |\\ CO\quad HO\end{matrix}$ is the one most likely respresenting this *iso*nitrosoketone.

It must not be overlooked, however, that another explanation of the isomerism among *iso*nitrosoketones would follow from the association of hydroxylic oxygen with carbonylic carbon in the one modification, and with azethenoid carbon in the other:

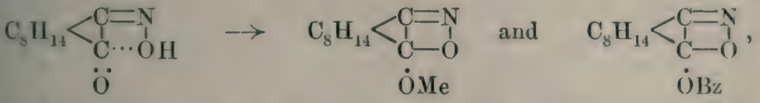


α-Benzilmonoxime.



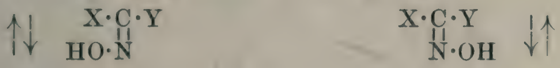
β-Benzilmonoxime.

This representation has the advantage of accounting for the conversion of the former substance into benzonitrile and benzoic acid, and would be in agreement with the structure already suggested for the *O*-methyl ether and colourless benzoyl derivative of *iso*-nitrosocamphor:

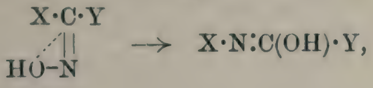


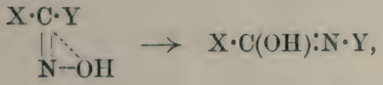
both of which yield α-camphornitrilic acid on hydrolysis.

The recognition of a union, slender and temporary perhaps, but still precise, brought about by the supplemental valency of the oxygen and the partial valency of the carbon, will, in addition to giving a material interpretation to the stereoisomerism of aldoximes, go some way towards explaining the Beckmann transformation of ketoximes. The net result of this well-known change is transposition of the hydroxyl group and the complex which finds itself in a situation sympathetic to that group:

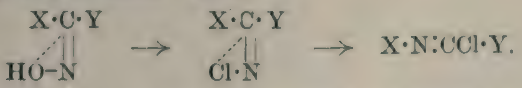


Now, supposing the hydroxylic oxygen to be already associated with azethenoid carbon, the complete transference of oxygen to carbon becomes more readily acceptable:

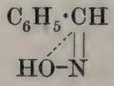


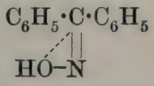


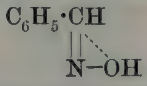
especially in the case when phosphorus pentachloride is the transforming agent, and it is supposed that the hydroxyl group is replaced by chlorine, this element resembling oxygen in being possessed of supplemental valency:



Independently of this attempt to apply a physical interpretation to the Hantzsch-Werner hypothesis, it remains a puzzling circumstance that benzophenoneoxime and camphoroxime should not yield a methyl derivative, particularly on recalling the facility with which benz*anti*aldoxime is methylated; for, on comparing the expressions,


Benz*anti*aldoxime.


Benzophenoneoxime.


Benz*syn*aldoxime.

it will be recognised that in benzophenoneoxime we have the counterpart of benz*anti*aldoxime and the antithesis of benz*syn*aldoxime; consequently, it would be natural to expect the latter to undergo methylation by diazomethane, which ought to leave benz*anti*aldoxime unchanged. Whether this abnormality betrays an inaccurate diagnosis of aldoxime configurations cannot be discussed at present, and the suggestion is too disconcerting for acceptance without comprehensive experimental evidence.

EXPERIMENTAL.

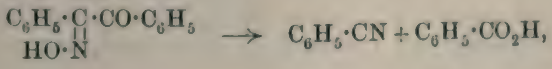
Preparation of the Aldoximes.

The *anti*aldoximes required for this investigation were prepared by the methods already familiar, the only new one being *p*-triazobenzaldoxime, for which we are indebted to Miss H. M. Judd. On converting the nitrobenz*anti*aldoximes into their *syn*-modifications, we experienced some difficulty in effecting the transformation by passing dry hydrogen chloride into an ethereal solution, but, on using chloroform in place of ether, and maintaining the temperature at 40—50°, satisfactory results followed, the *syn*-oxime being obtained in each case on decomposing the precipitated hydrochloride with sodium carbonate. It was early recognised, however, that the nitrobenz*syn*aldoximes described in the literature were actually mixtures of both isomerides, and it became necessary to adopt certain devices in crystallisation to prevent regeneration of the *anti*-modification, which appears to take place with greater readiness than has been supposed. The *o*-nitro-compound, for example, stated by Goldschmidt and van Rietschoten (*Ber.*, 1893, **26**, 2101) to crystallise from warm benzene in prisms melting at 136°, was found by us to melt at 154°; this melting point was reached by dissolving the substance as quickly as possible in benzene at 30°, cooling the liquid immediately, and removing the crystals without delay. The *m*-nitrobenz*syn*aldoxime was precipitated by petroleum from a freshly prepared solution in warm ethyl acetate, and then melted at 123°, instead of 116—118° as recorded by Goldschmidt (*Ber.*, 1890, **23**, 2170), who used ether. *p*-Nitrobenz*syn*aldoxime was dissolved in cold acetone, and precipitated by water, when it melted at 182—184°, whence the oxime described by Goldschmidt and Kjellin (*Ber.*, 1891, **24**, 2550) would appear to have contained some *anti*-modification, since their product melted at 170—176°, whilst Behrend and Konig (*Annalen*, 1891, **263**, 350) record 173—175° as the melting point; the necessity of immediate precipitation was further established by the fact that crystals deposited during the next half-hour by the filtrate from the first crop melted at 175—177°.

Preparation of the Benzilmonoximes.

The experiments of Meyer and Auwers (*Ber.*, 1889, **22**, 540) showed that hydroxylamine hydrochloride converts benzil chiefly into the β-monoxime, the proportion of which is directly dependent on the temperature of the system and the period of association, so that the β-monoxime becomes the sole product after twenty-four hours at the laboratory temperature. When the free base is employed without heating, there is produced a mixture of α- and β-monoximes, from which the latter is removed by washing with cold benzene, but this process for isolating the α-monoxime is a somewhat tedious one, and we have found the following more convenient. Seven grams of powdered hydroxylamine hydrochloride were covered with 50 c.c. of dry pyridine, and stirred with 5 grams of powdered sodium hydroxide until decomposition appeared complete; the filtered liquid, mixed with 20 grams of benzil dissolved in 50 c.c. of pyridine, was treated with one drop of a 50 per cent. solution of potassium hydroxide, and after twenty-four hours at the laboratory temperature was diluted largely with water and nearly neutralised with dilute acetic acid. One crystallisation of the precipitate from 30 per cent. alcohol was sufficient to raise the melting point to the right temperature, 137°.

In connexion with the relative stability of the two benzilmonoximes, a curious difference has been observed. Whilst the α-oxime may be kept indefinitely without undergoing alteration, the β-modification is very sensitive to the combined action of light and air. From the same specimen of this material, two bottles were filled, one completely, the other to about one-tenth of its capacity, the two bottles being then exposed side by side in a south aspect during the past eighteen months, out-of-doors, but protected from rain. The oxime in the first bottle has remained unchanged, but the substance in the bottle which was nearly empty became brown in the course of the first five weeks, gradually developing a strong odour of benzonitrile, whilst crystals of benzoic acid sublimed in the vessel. Although the production of these compounds might arise from auto-oxidation,



$$\begin{array}{l}C_6H_5\cdot C\cdot CO\cdot C_6H_5\\ \qquad\;\;\,\|\\ \quad HO\cdot N\end{array} \longrightarrow C_6H_5\cdot CN + C_6H_5\cdot CO_2H,$$

it is nevertheless clear that atmospheric oxygen is involved, because on opening the inverted bottle under water the latter rose approximately one-fifth in the vessel; moreover, if auto-oxidation alone had occurred, the α-oxime would be expected to undergo this change more readily than the isomeride.

Recalling the marked colour-difference in alkaline solutions of the two *iso*nitrosocamphors, of which the unstable modification develops a deep orange coloration, that of the stable form being canary-yellow, 0·5 gram of each benzilmonoxime was dissolved in 5 c.c. of a 10 per cent. solution of potassium hydroxide; the α-oxime (unstable) formed a deep orange solution, whilst that of the β-modification was canary-yellow.

Action of Diazomethane on the Oximes.

The behaviour of the oximes towards diazomethane having been studied under conditions which were, as far as possible, strictly comparable, it is only necessary to describe one experiment in any detail. Half a gram of *p*-nitrobenz*anti*aldoxime dissolved in pure dry ether was mixed with an ethereal solution of diazomethane prepared from 2·5 c.c. of methylnitrosourethane; after twenty-four hours, when the solution was no longer yellow, the solvent was evaporated by a current of dry air, and the solid residue treated with a further quantity of diazomethane in ether. Another interval of twenty-four hours having elapsed, and the liquid still being yellow, the flocculent suspension of polymethylene was filtered, and the solvent evaporated as before. The residue was then taken up with a small quantity of ether and shaken with successive quantities of a 5 per cent. solution of potassium hydroxide until the latter was colourless, when the ethereal solution was transferred to a distilling flask, from which the dissolved material was removed with steam; the solid distillate melted at 103°, weighed 0·2 gram, and did not depress the melting point of a specimen of the methyl ether prepared from *p*-nitrobenz*anti*aldoxime by an ordinary method. On recrystallisation from boiling water, the melting point was raised to 105°, that recorded by Goldschmidt and Kjellin being 101°.

Before applying this process to the other oximes, these were tested as to their volatility in steam, and also as to their extractibility by ether from solutions in dilute alkali, and in the case of the *p*-triazobenzaldoximes, both of which are volatile, the distillate was treated with alkali before deciding whether methylation had occurred. In this manner, definite results have been obtained with five pairs of oximes, as already summarised; camphoroxime and benzophenoneoxime did not undergo any change, the residue left on evaporating the solvent melting in each case within two or three degrees of the purified material, which was recovered by one crystallisation from a suitable solvent.

In the case of α-benzilmonoxime, the residue on removing ether after double treatment with diazomethane was a viscous, golden oil. This was re-dissolved in a small quantity of ether, and shaken several times with dilute potash, from which a small proportion of unchanged oxime was afterwards precipitated by carbon dioxide. The residue then left by the ether had the same appearance as before:

0·1838 gave 9·6 c.c. N_2 at 18·5° and 737 mm. N = 5·89.
$C_{15}H_{13}ON$ requires N = 5·86 per cent.

The amount at our disposal was too small to admit of detailed examination, but the presence of a *N*-methyl ether was indicated by the behaviour of the substance on treatment with hydrochloric acid, because on removing undissolved material by ether and adding sufficient alkali to neutralise the acid, Fehling's solution was reduced without heating. A blank experiment with the original oxime gave a negative result, as also the oil from β-benzilmonoxime and diazomethane; furthermore, the unmethylated oxime recovered from this latter experiment was found to consist of the β-isomeride, which therefore is not transformed into the α-modification.

The experiments with the two *iso*nitrosocamphors have been already described.

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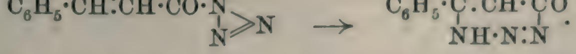
LII.—*The Triazo-group. Part IX. Transformation of Cinnamoylazoimide into Cinnamenylcarbimide (Cinnamenyl* iso*Cyanate).*

By Martin Onslow Forster.

Recent observations connected with the triazo-group appeared to justify the expectation that in appropriate circumstances it might be possible to transform cinnamoylazoimide into the isomeric ketone of phenyldihydrotriazine:



$$C_6H_5\cdot CH{:}CH\cdot CO\cdot\begin{matrix}N\\|\\N\end{matrix}\!\!>\!N \longrightarrow \begin{matrix}C_6H_5\cdot C{:}CH\cdot CO\\|\qquad\qquad|\\NH\cdot N{:}N\end{matrix}.$$

The acyl azide was accordingly prepared by the interaction of cinnamoyl chloride and sodium azide, but has not shown a tendency to undergo the above re-arrangement.

I should not have dealt further with this material, belonging as it does to a class of which the investigation relates so conspicuously to the province of Geheimrath Professor Curtius, had it not been for an accidental observation which offers the explanation, not hitherto advanced, of numerous changes described by that chemist. One of the most characteristic features of the acyl azides is their behaviour towards water, alcohols, and amines (Curtius, *Ber.*, 1894, **27**, 778), which take part in the following reactions:

$$X\cdot CO\cdot N_3 + H_2O = N_2 + X\cdot NH\cdot CO\cdot OH.$$
$$X\cdot CO\cdot N_3 + Y\cdot OH = N_2 + X\cdot NH\cdot CO\cdot OY.$$
$$X\cdot CO\cdot N_3 + Y\cdot NH_2 = N_2 + X\cdot NH\cdot CO\cdot NHY.$$

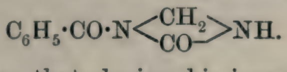
Since this series was brought to light by Curtius in connexion with benzoylazoimide, the same observer has described a large number of acyl azides, and has shown that the majority conform to the generalisation quoted, but in no case, so far as I have been able to ascertain, has it been pointed out that the changes in question are not specific effects of water, alcohols, and amines, but owe their occurrence to preliminary transformation of the azoimide into carbimide:

$$X\cdot CO\cdot N_3 \longrightarrow N_2 + X\cdot N{:}C{:}O,$$

which then acts in the normal manner on the base or hydroxy-compound present in the system. This conclusion follows from the behaviour of cinnamoylazoimide, which, when heated in dry benzene at a temperature somewhat below the boiling point of the hydrocarbon, steadily loses nitrogen, leaving cinnamenylcarbimide in solution; on removing benzene, the *iso*cyanate may be distilled as a colourless liquid which is almost odourless until warmed, when the penetrating odour characterising members of the carbimide group becomes perceptible, associated with a suggestion of cinnamon.

Although a large number of acyl azides have been shown to yield, under the influence of amines and hydroxy-compounds, the derivatives to be expected from the corresponding *iso*cyanate, this appears to be the first case in which that intermediate compound has been recognised. On one occasion, at least, it has probably been isolated, because Curtius (*J. pr. Chem.*, 1895, [ii], **52**, 265) records the formation of a substance arising from hippurylazoimide by elimination of nitrogen when the solution in dry benzene is boiled; this compound, which melted at 98°, gave 16·01 per cent. of nitrogen on analysis, and is therefore most likely to have been hippenylcarbimide, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot N{:}C{:}O$, which contains 15·91 per cent., but its properties were not studied, and the composition

$C_9H_6ON_2$ was assigned to it. Another substance described by Curtius in the same communication melted at 233°, and gave analytical results in agreement with the figures required by hippenylcarbimide; it was obtained by the action of hot water on hippurylazoimide, and is referred to as being "perhaps the carbanil of hippuric acid, $C_6H_5\cdot CO\cdot NH\cdot CH_2\cdot N{:}CO$, or more probably a polymeride of this," but no further steps were taken to establish its identity. The high melting point of this compound suggests the possibility of action having occurred between the imino-group and the *iso*cyanate radicle, leading to



$$C_6H_5\cdot CO\cdot N{<}\begin{matrix}CH_2\\CO\end{matrix}{>}NH.$$

It is significant also that during his investigation of numerous members of the polypeptide class, Curtius frequently noted that the oily residue remaining when the complex azoimides were heated sufficiently to lose two-thirds the azidic nitrogen became solid on cooling (*J. pr. Chem.*, 1904, [ii], **70**, 79, 212, 249), these materials doubtless consisting of the carbimides. Elimination of nitrogen from an acyl azide in presence of some indifferent solvent having a suitable boiling point should thus afford an unusually simple and convenient method of preparing the *iso*cyanates of sensitive or elaborate molecules.

The explanation here assigned to the mechanism of azide-transformation is not at variance with any of the other observations made by Curtius in this group. The alternative action of bases, for instance, by which in ether the azides are made to appear as acylating agents:

$$C_6H_5\cdot CO\cdot N_3 + NH_2\cdot C_6H_5 = C_6H_5\cdot CO\cdot NH\cdot C_6H_5 + HN_3,$$

is doubtless permitted by the circumstance that the temperatures reached in the solvent mentioned are too low to involve loss of nitrogen, and similar conditions prevail in the numerous cases of polypeptide formation accomplished by the action of acyl azides on amino-esters in presence of cold dilute alkali; in these changes the acyl azide is the analogue of an acyl chloride. The apparently abnormal behaviour of carbonyl bisazide, or carbazide (Curtius, *J. p. Chem.*, 1895, [ii], **52**, 458), and of carbamic azide (*ibid.*, 468) towards boiling water, which resolves them into carbon dioxide and hydrazoic acid, is at once explained by considering the structure of these compounds:

$$N_3\cdot CO\cdot N_3 \text{ and } N_3\cdot CO\cdot NH_2,$$

since *iso*cyanates could not be expected from them; moreover, the carbamic derivative is indifferent towards boiling alcohol. It is recorded also by Curtius and Lorenzen (*J. pr. Chem.*, 1898, [ii], **58**, 165) that in contrast with the azides of carboxylic acids, the sulphonic azides are not decomposed when heated with water or alcohol, and this immunity is not surprising when the unlikely character of the transformation,

$$C_6H_5\cdot SO_2\cdot N_3 \longrightarrow N_2 + C_6H_5\cdot N{:}SO_2,$$

is considered. Furthermore, phenylcarbamic azide is another substance escaping azide-transformation, hot water effecting hydrolysis, whilst phenylcarbamic ester and diphenylcarbamide are produced by alcohol and aniline respectively (Curtius and Burkhardt, *J. pr. Chem.*, 1898, [ii], **58**, 207); in this instance, also, the abnormal course is the only possible one when it is recalled that the transformation

$$C_6H_5\cdot NH\cdot CO\cdot N_3 \longrightarrow N_2 + C_6H_5\cdot NH\cdot N{:}C{:}O$$

would be involved by adherence to the rule. Finally, oxalic azide, $N_3\cdot CO\cdot CO\cdot N_3$, is merely hydrolysed instead of yielding a carbamide derivative, as might be anticipated from the difficulty of producing carbiminic *iso*cyanate, $O{:}C{:}N-N{:}C{:}O$.

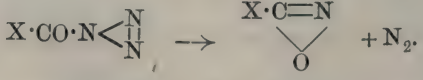
Several chemical changes may be adduced as analogous to the transformation of an acyl azide into the corresponding carbimide, the best known being the Hofmann reaction for the preparation of amines:

$$X\cdot CO\cdot NHBr - HBr = X\cdot N{:}C{:}O.$$
$$X\cdot CO\cdot N{:}N_2 - N_2 = X\cdot N{:}C{:}O.$$

Here, as in the case under consideration, the violent disturbance of chemical affinity attendant on the removal of two atoms from association with the nitrogen in direct linking with the main part of the system, has caused that element to change places with the neighbouring carbon atom, and the same thing occurs when benzylazoimide is decomposed by acids (Curtius and Darapsky, *J. pr. Chem.*, 1901, [ii], **63**, 428):

$$C_6H_5\cdot CH_2\cdot N_3 - N_2 = C_6H_5\cdot N{:}CH_2.$$

The analogy offered by benzylazoimide is unfavourable to the interesting suggestion of Wieland (*Ber.*, 1909, **42**, 807), that azide-transformation may be preceded by production of a nitrile-oxide:



It would appear, also, that the alteration undergone by acyl derivatives of hydroxamic acids (Thiele and Pickard, *Annalen*, 1899, **309**, 189) may be classified with the foregoing, although the mechanism of this particular case is not so apparent; nevertheless, alkyl carbamates result from the action of boiling alcohol on these substances, suggesting the formation of the carbimide as an intermediate stage:

$$X\cdot C(OH){:}N\cdot OAc \longrightarrow X\cdot CO\cdot NH\cdot OAc.$$
$$X\cdot CO\cdot NH\cdot OAc - H\cdot OAc = X\cdot N{:}C{:}O.$$

Furthermore, it has been shown recently by Darapsky (*J. pr. Chem.*, 1907, [ii], **76**, 433; *Ber.*, 1907, **40**, 3033) that sodium hypochlorite oxidises hydrazodicarbonamide to hydrazoic acid, and converts phenylsemicarbazide into phenylazoimide, doubtless owing to intermediate formation of azodicarbonamide and phenylazocarbonamide respectively. It seems highly probable that these are further illustrations of the same principle, for, taking the simpler case, that of phenylazocarbonamide,

$$C_6H_5\cdot N{:}N\cdot CO\cdot NH_2 - H_2 = C_6H_5\cdot N{:}N\cdot N{:}C{:}O,$$

it may be that removal of hydrogen by the hypochlorite leads to the hypothetical substance above indicated, which might easily pass into phenylazoimide by further oxidation; this explanation, although different from the one put forward by Darapsky, has not the drawback of depending on phenyltriazen as an intermediate compound.

EXPERIMENTAL.

Cinnamoylazoimide, $C_6H_5\cdot CH{:}CH\cdot CO\cdot N_3$.

Twenty-five grams of finely powdered sodium azide were added to 50 grams of cinnamoyl chloride, dissolved in 300 c.c. of dry ether, and gently agitated during six hours; the cinnamoylazoimide being only moderately soluble in ether, the suspended solid was filtered, extracted with cold water, and then dried previous to being purified by precipitation with petroleum from benzene solution. When recrystallised from boiling petroleum (60—80°), it formed large, lustrous, six-sided plates melting at 86° with liberation of nitrogen:

0·1066 gave 22·6 c.c. N_2 at 20° and 760 mm. N = 24·25.
$C_9H_7ON_3$ requires N = 24·28 per cent.

The substance is freely soluble in cold benzene, ethyl acetate, acetone, or chloroform, and dissolves readily in cold alcohol; it effervesces vigorously with concentrated sulphuric acid, and is hydrolysed by alcoholic potash to cinnamic and hydrazoic acids without loss of nitrogen. A solution in acetone was exposed to light during five weeks without molecular re-arrangement on the part of the azide.

Cinnamenylcarbimide (*Cinnamenyl* iso*Cyanate*), $C_6H_5{\cdot}CH{:}CH{\cdot}N{:}C{:}O$.

The disengagement of nitrogen which takes place at the melting point of cinnamoylazoimide leads, as has been stated, to the production of cinnamenyl *iso*cyanate, but even with small quantities of material this alteration is liable to pass beyond control; the carbimide was therefore prepared in the following manner.

Five grams of cinnamoylazoimide, covered with 25 c.c. of benzene dried over sodium, were heated in a Wurtz flask under reflux, the whole apparatus having been thoroughly dried and protected from atmospheric moisture by a tube of calcium chloride at the exit of the condenser; the colourless solution rapidly became pale yellow, and bubbles of gas appeared, the heating being continued below the boiling point of the hydrocarbon until decomposition seemed complete. Another quantity of 5 grams having been added and decomposed in the same way, the benzene was distilled off on the water-bath, and the residue boiled under 12 mm. pressure, the distillate passing over steadily at 107°:

0·2219 gave 19·4 c.c. N_2 at 20° and 758 mm. N = 9·98.

C_9H_7ON requires N = 9·65 per cent.

Cinnamenylcarbimide is a colourless, refractive liquid, having a faint, cinnamic odour, and but little suggestion of the *iso*cyanate group until warmed with water, when the vapour becomes overpowering; the density is 1·101 at 17° compared with water at the same temperature.

Derivatives of Cinnamenylcarbimide.

Methyl cinnamenylcarbamate, $C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2{\cdot}CH_3$, crystallises from benzene in lustrous plates melting at 126°:

0·2018 gave 14·6 c.c. N_2 at 17° and 755 mm. N = 8·33.

$C_{10}H_{11}O_2N$ requires N = 7·91 per cent.

It is freely soluble in cold acetone or ethyl acetate, less readily in chloroform, methyl alcohol, or ethyl alcohol, and still less freely in cold benzene, whilst boiling petroleum dissolves it sparingly. Evidently the same substance was obtained by Thiele and Pickard (*Annalen*, 1899, **309**, 196) on decomposing acyl derivatives of cinnamhydroxamic acid with methyl alcohol, but 115° is the melting point recorded by these authors.

Ethyl cinnamenylcarbamate, $C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2{\cdot}C_2H_5$, also prepared by Thiele and Pickard, is described by them as melting at 89°. It crystallises from boiling petroleum in opaque, centimetre-long, snow-white needles, the melting point of which could not be raised above 87°, even by recrystallisation from alcohol followed by petroleum; it acquires the odour of benzaldehyde during the course of a few weeks if preserved in a stoppered bottle.

Cinnamenylphenylcarbamide, $C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, prepared from cinnamenylcarbimide and aniline in benzene, is moderately soluble in boiling alcohol, from which it separates in transparent, colourless prisms melting at 217°:

0·2007 gave 21·2 c.c. N_2 at 21° and 767 mm. N = 12·14.

$C_{15}H_{14}ON_2$ requires N = 11·77 per cent.

It is insoluble in boiling petroleum and in cold benzene, dissolving very sparingly in the latter on boiling.

Cinnamenylpiperidylcarbamide, $C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO{\cdot}N{\cdot}C_5H_{10}$, is freely soluble in hot benzene, from which it separates in colourless nodules melting at 140°:

0·1845 gave 18·9 c.c. N_2 at 18° and 776 mm. N = 12·08.

$C_{14}H_{18}ON_2$ requires N = 12·17 per cent.

The substance is freely soluble in cold acetone, chloroform, ethyl acetate, methyl alcohol, or ethyl alcohol, but dissolves very slightly in boiling petroleum; in concentrated sulphuric acid it develops a magenta coloration. During a few weeks in a stoppered bottle the substance changed to a pasty, yellow mass, with a faint odour of benzaldehyde.

sym-*Cinnamenylphenylsemicarbazide*,

$$C_6H_5{\cdot}CH{:}CH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5,$$

separates immediately on adding phenylhydrazine to the calculated amount of cinnamenylcarbimide in benzene:

0·1736 gave 25·2 c.c. N_2 at 19° and 776 mm. N = 17·04.

$C_{15}H_{15}ON_3$ requires N = 16·60 per cent.

The compound is insoluble in boiling petroleum, and dissolves only sparingly in boiling benzene or absolute alcohol; it is somewhat more readily soluble in boiling acetone, from which it separates in minute, snow-white needles melting and evolving gas at 221°.

I desire to express my indebtedness to Mr. Robert Müller for the analytical operations connected with this work.

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SOUTH KENSINGTON, S.W.

LIII.—*Note on the Detection of White or Ordinary Phosphorus in the Igniting Composition of Lucifer Matches.*

By Thomas Edward Thorpe, C.B., F.R.S.

Act 8 Edward 7 Ch. 42, known as the White Phosphorus Matches Prohibition Act, 1908, which comes into operation on January 1, 1910, enacts that it shall not be lawful for any person to sell or to expose for sale or have in his possession for the purposes of sale any matches made with white phosphorus; and that it shall not be lawful to import into the United Kingdom matches made with white phosphorus, and that matches so made shall be included in the table of prohibitions and restrictions contained in Section 42 of the Customs Consolidation Act, 1876.

As the new Act will throw upon the Inspectors under the Factory and Workshop Act, 1901, the duty of taking, from time to time, samples of the materials in use at match factories, and will require Officers of Customs to sample imported matches, I have thought it desirable to examine the methods by which the presence of ordinary phosphorus in the igniting composition of lucifer matches may with certainty be established. At first sight this would seem to be a very simple problem, and the application of the well-known Mitscherlich test for free phosphorus would appear to be all that is required.

In reality, however, this test is not generally applicable, owing to the fact that the igniting composition very frequently contains phosphorus sesquisulphide, which, in certain circumstances, may give rise to a luminous glow (compare Scharff, *Zeitsch. physikal. Chem.*, 1908, **62**, 179; Clayton, Proc., 1902, **18**, 129, and 1903, **19**, 231; Mai and Schaffer, *Ber.*, 1903, **36**, 870; Vignon, *Compt. rend.*, 1905, **140**, 1449; Siemens, *Chem. Zeit.*, 1906, **30**, 263 and 271; Schenck and Scharff, *Ber.*, 1906, **39**, 1522; Aronstein, *Chem. Centr.*, 1906, i, 1906, from *Chem. Weekblad*, 1906, **3**, 283, and *Chem. Centr.*, 1906, ii, 977, from *Chem. Weekblad*, 1906, **3**, 490). Mistakes have already occurred at Continental ports of entry in consequence of the application of the Mitscherlich test.

The most direct and most certain method of establishing the presence of ordinary phosphorus in the igniting composition is to isolate the phosphorus as such, and this may readily be effected by placing the "composition," either as dried paste, or as it exists on the heads of the matches, in a small bulb tube, which, after being exhausted, is gently heated so as to volatilise the phosphorus, which can thus be obtained as a colourless, lustrous, crystalline sublimate, the physical characteristics of which are quite sufficient to identify it (compare W. Flight, Douglas Hermann, and Story-Maskelyne, *Ber.*, 1873, **6**, 1415; *Jahresber.*, 1873, 221).

In practice the method is carried out as follows:

A few grams of the composition, or, in the case of finished matches, the heads cut from a couple of hundred of the splints, are placed over concentrated sulphuric acid in a desiccator, filled with carbon dioxide, at the ordinary temperature until thoroughly dry. The dried material is then transferred to a bulb of 25 c.c. capacity blown on the end of a tube of 15 mm. diameter, and 20 cm. long. A bulb of this capacity will hold from 300 to 400 match-heads. The apparatus is filled with dry carbon dioxide, and is evacuated as completely as possible, most conveniently by means of a Fleuss or Gaede pump, and the end sealed off. The bulb is then gently heated at from 40° to 60° for a couple of hours, when the phosphorus, if present, will be volatilised and will be condensed in the cold upper part of the tube as a lustrous, transparent, highly refractive sublimate of octahedral or dodecahedral crystals, which increase in size after standing a few days, and preserve their lustre and transparency unchanged if protected from light.

A very small admixture of white phosphorus can be detected in this manner. Matches made with phosphorus sesquisulphide, although affording a luminous glow, give no sublimate of any kind under these conditions.

I have to thank Mr. Jacob Fox, B.Sc., for his assistance in carrying out the experimental work required to prove the validity of this method.

GOVERNMENT LABORATORY.

LIV.—*Salicylidene*-m-*toluidine, a New Phototropic Compound; Salicylideneamines: Salicylamides.*

By ALFRED SENIER and FREDERICK GEORGE SHEPHEARD.

IN the course of a search for methods of acridine synthesis which might lead to the discovery of types of acridines at present unknown, it seemed probable, as in the case of other methods of acridine synthesis (Senier and Goodwin, Trans., 1902, **81**, 281), that the compounds described in this paper would condense more readily, yielding acridines or acridones, than the simpler homologues from which

Pictet and Ankersmit (*Annalen*, 1891, **266**, 138) and Pictet and Hubert (*Ber.*, 1896, **29**, 1189) showed that acridines could be obtained. Contrary to our expectation, however, the only acridine derivative isolated was an acridone obtained from one of the simpler homologues.

One of the salicyl derivatives prepared, namely, salicylidene-*m*-toluidine, exhibited that most remarkable photo-reaction which Marckwald (*Zeitsch. physikal. Chem.*, 1899, **30**, 140) has named phototropy. On crystallisation from its solutions, the crystals are, in the first place, pale yellow, but when exposed to sunlight the colour changes quickly to deep orange, and this colour change is reversed, although much more slowly, when the crystals are placed in the dark. Spectroscopic experiments showed that the change from the paler-coloured to the darker-coloured modification is due to the activity of the light waves of high refrangibility. This change does not take place in solution, in which condition only the paler-coloured modification appears to exist. Specimens prepared a month ago retain their photo-reactive sensibility unimpaired. After exposure to the light of an arc lamp, no phosphorescence was observed on the sudden removal of the source of light. Rubbing between glass plates in a dark room gave no indication of triboluminescence. It is noteworthy that the other condensation products of salicylaldehyde with similar amines described in this paper are not phototropic. This property of salicylidene-*m*-toluidine is similar to that originally investigated by Marckwald in the case of the anhydrous chloride of quinoquinoline and in that of β-tetrachloro-α-ketonaphthalene. It is similar also to that exhibited by the derivatives of fulgenic acid described by Stobbe (*Annalen*, 1908, **359**, 1) in an important contribution to the study of phototropy, which contains also full references to previous work on this subject.

Probably, in accordance with the conclusion arrived at by Stobbe in the case of the compounds he studied, phototropy in this instance, also, depends on the existence of two stereo- or other isomerides, formed respectively under the influence of short or long waves of light.

These experiments are being continued with the view of determining the character of the isomerism exhibited, and of obtaining, among analogous compounds, further instances of phototropy which might lead to the elucidation of the relation of this phenomenon to molecular constitution.

1. *Salicylideneamines.*

The salicylideneamines described below are readily formed by the condensation of salicylaldehyde with the respective bases; in some instances the action took place without the application of heat, in others gentle warming was found necessary.

*Salicylidene-*m*-toluidine*, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_4Me$.—This compound exhibits the reversible photo-reaction already described.

The crude product of the condensation was dissolved in methyl alcohol, which on evaporation gradually deposited clusters of prisms of the compound. It dissolves very readily in the usual organic solvents. It melts at 39·5° (corr.):

0·2151 gave 12·5 c.c. N_2 (moist) at 13° and 753 mm. N = 6·80.

$C_{14}H_{13}ON$ requires N = 6·64 per cent.

*Salicylidene-*m*-4-xylidine*, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_3Me_2$, consists of bright yellow needles, which readily dissolve in most organic solvents. It melts at 30—31° (corr.):

0·2638 gave 13·9 c.c. N_2 (moist) at 14° and 764 mm. N = 6·23.

$C_{15}H_{15}ON$ requires N = 6·22 per cent.

*Salicylidene-*p*-xylidine*, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_3Me_2$, crystallises from dilute alcohol in glistening, yellow plates. It dissolves readily in the usual organic solvents, and melts at 107—108° (corr.):

0·2258 gave 12·3 c.c. N_2 (moist) at 13° and 750 mm. N = 6·35.

$C_{15}H_{15}ON$ requires N = 6·22 per cent.

Salicylidene-ψ-cumidine, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_6H_2Me_3$, was obtained in long, brilliant yellow needles from solution in dilute alcohol. It dissolves easily in the usual organic solvents, and melts at 71° (corr.):

0·2125 gave 10·8 c.c. N_2 (moist) at 16° and 767 mm. N = 5·98.

$C_{16}H_{17}ON$ requires N = 5·86 per cent.

Salicylidene-α-naphthylamine, $OH\cdot C_6H_4\cdot CH\colon N\cdot C_{10}H_7$, crystallises from methyl alcohol in dark orange prisms. It is very soluble in the usual organic solvents, and melts at 45·5° (corr.):

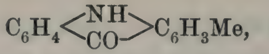
0·2930 gave 13·7 c.c. N_2 (moist) at 10·5° and 766 mm. N = 5·63.

$C_{17}H_{13}ON$ requires N = 5·67 per cent.

2. *Salicylamides.*

In the preparation of the following salicylamides, salicylic acid (1 mol.) and the respective amine (1 mol.) were warmed at 100° in an open vessel, and phosphorus trichloride in slight excess was dropped on the mixture. When the evolution of hydrogen chloride had ceased, the hot liquid was poured into water, when it solidified. It was then triturated with more water, dissolved in a cold dilute solution of sodium hydroxide, and carbon dioxide passed through the solution. By this means a precipitate was obtained free from unaltered salicylic acid or amine. The product was finally recrystallised from alcohol. Two recrystallisations were generally found sufficient.

The salicylamides were each submitted to the action of heat, alone, and in the presence of various condensing agents. In the case of salicyl-*m*-toluidide a very small yield of the corresponding acridone was obtained.

2-(or 4-)*Methylacridone*,  $C_6H_4\!<\!\substack{NH\\CO}\!>\!C_6H_3Me$, was purified by sublimation, when it consists of yellow, feathery crystals. It melts at 312° (uncorr.):

Found, $C = 80{\cdot}26$; $H = 5{\cdot}93$.

$C_{14}H_{11}ON$ requires $C = 80{\cdot}38$; $H = 5{\cdot}26$ per cent.

In the case of the distillation of the higher salicylamides the reaction is of a different nature, the decomposition which takes place results in each case in the liberation of a large proportion of the amine.

Salicyl-m-*toluidide*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$, consists of small, colourless prisms, readily soluble on warming in alcohol, benzene, chloroform, light petroleum or glacial acetic acid. It melts at 135—136° (corr.):

0·4036 gave 21·9 c.c. N_2 (moist) at 12° and 745 mm. $N = 6{\cdot}31$.

$C_{14}H_{13}O_2N$ requires $N = 6{\cdot}17$ per cent.

Salicyl-m-4-*xylidide*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me_2$, crystallises in colourless needles, which dissolve readily in alcohol, ethyl acetate, chloroform or benzene, sparingly in light petroleum or ether. It melts at 143° (corr.):

0·3698 gave 19·2 c.c. N_2 (moist) at 14° and 746 mm. $N = 5{\cdot}99$.

$C_{15}H_{15}O_2N$ requires $N = 5{\cdot}81$ per cent.

Salicyl-p-*xylidide*, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me_2$, occurs in large, well-defined, colourless prisms, which are very slightly soluble in benzene, chloroform or light petroleum, readily so in alcohol, acetone or ethyl acetate. It melts at 164° (corr.):

0·1513 gave 0·4161 CO_2 and 0·0880 H_2O. $C = 74{\cdot}92$; $H = 6{\cdot}51$.

$C_{15}H_{15}O_2N$ requires $C = 74{\cdot}66$; $H = 6{\cdot}27$ per cent.

Salicyl-ψ-cumidide, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_2Me_3$, consists of colourless needles, sparingly soluble in ether or benzene, soluble in alcohol or chloroform, very soluble in acetone. It melts at 188—189° (corr.):

0·1988 gave 0·5437 CO_2 and 0·1219 H_2O. $C = 74{\cdot}64$; $H = 6{\cdot}86$.
0·2474 „ 11·9 c.c. N_2 (moist) at 13° and 764 mm. $N = 5{\cdot}71$.

$C_{16}H_{17}O_2N$ requires $C = 75{\cdot}26$; $H = 6{\cdot}72$; $N = 5{\cdot}49$ per cent.

Salicyl-α-naphthalide, $OH{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, crystallises in colourless prisms, which dissolve sparingly in light petroleum and readily in alcohol. It melts at 182—183° (corr.):

0·2923 gave 13·2 c.c. N_2 (moist) at 16° and 770 mm. N = 5·34.

$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

Salicyl-β-naphthalide, $OH\cdot C_6H_4\cdot CO\cdot NH\cdot C_{10}H_7$, forms colourless, silky needles, soluble in alcohol, which melt at 188—189° (corr.):

0·2499 gave 11·8 c.c. N_2 (moist) at 18° and 759 mm. N = 5·44.

$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

The ***sodium*** derivative, $ONa\cdot C_6H_4\cdot CO\cdot NH\cdot C_{10}H_7,5H_2O$, is deposited in rosettes of small, colourless needles when a solution of salicyl-β-naphthalide in sodium hydroxide is allowed to stand. It is very slightly soluble in cold water, and hydrolyses on warming; it dissolves readily in alcohol:

0·3259, dried at 105°, lost 0·0761. H_2O = 23·35.

0·3259 gave 0·0601 Na_2SO_4. Na = 5·97.

$C_{17}H_{12}O_2NNa,5H_2O$ requires H_2O = 24·00; Na = 6·13 per cent.

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LV.—*The Atomic Volumes of Phosphorus. Part II. Phosphorus and Bromine.*

By EDMUND BRYDGES RUDHALL PRIDEAUX.

IN a former paper (Trans., 1907, **91**, 1711) a comparison was made between the atomic volumes of phosphorus and chlorine before and after combination, and it was there shown that, assuming chlorine to possess its elementary atomic volume in phosphorus tri- and pentachlorides, the atomic volume of phosphorus in the latter is much less, and in the former greater, than that of the element.

These data have now been extended by a measurement of the specific volumes of phosphorus pentabromide at various temperatures, and in order to obtain a comparison temperature, the vapour pressures of this compound have been determined.

Expansion of Phosphorus Pentabromide.—Some of Merck's purest preparation was analysed, the bromine being determined as silver bromide and the phosphorus as magnesium pyrophosphate with the following results:

Found, Br = 92·3; P = 7·7.

PBr_5 requires Br = 92·7; P = 7·3 per cent.

The bulb of the dilatometer employed had a capacity of about 0·4 c.c. The capacity of each mm. length of the stem was 0·001 c.c. Corrections were made for inequalities in the bore and for the expansion of the glass.

The approximate specific volume of liquid phosphorus pentabromide having been ascertained, the calculated amount of the substance was introduced into the dilatometer, which was then evacuated, sealed, and weighed. The volumes at various temperatures were read in baths of sulphuric acid and glycerol. Afterwards the tube was carefully broken, boiled with nitric acid, dried, and weighed.

Two sets of observations were made with different quantities of phosphorus pentabromide, with the results tabulated below. When temperatures were plotted against scale divisions of the dilatometer, it was seen that the expansion was uniform from 85° to 100°. An inflexion then appeared, similar to that seen in the case of sulphur at 159°. The expansion then again proceeded uniformly at a lower rate.

To give an idea of the degree of accuracy with which the readings could be taken, it may be stated that 15 per cent. of these lay on the two straight lines within 0·1 scale-divisions or $\frac{1}{400}$ of the total volume, and 85 per cent. within 0·05 scale-divisions or $\frac{1}{800}$ of the total volume.

The following are some experimental values of the specific volumes from experiments I and II, allowing in each case for inequalities of bore of the capillary tube and expansion of glass.

	I. Weight of $PBr_5=1·423$.		II. Weight of $PBr_5=1·167$.		
Temp.	Spec. vol.	Mol. vol.	Spec. vol.	Mol. vol.	Mean mol. vol.
85°	0·3530	152·1	0·3522	151·7	151·9
100	0·3621	156·0	0·3627	156·3	156·1
130	0·3755	161·7	0·3757	161·8	161·8
165	0·3899	168·0	0·3906	168·3	168·2

From these and the other observations, the expansion of phosphorus pentabromide was calculated as below:

(1) 85—100° $V_t=V_{85^\circ}(1+0·0019t^\circ)$.

(2) (100—165°) $V_t=V_{100^\circ}(1+0·0012t^\circ)$.

In order to compare the molecular volumes of phosphorus pentabromide with those of other phosphorus compounds under conditions of equal vapour pressure, it is at least necessary to know the boiling point of the former. This, however, is inaccessible to direct measurement. All the methods of determining vapour pressures are out of the question, either on account of the action of phosphorus pentabromide on mercury or on account of the dissociation of the vapour at diminished pressures. A method was therefore devised by which the vapour pressure is measured in a confined space in such a way that the total pressure is never less than atmospheric and no distillation takes place.

Briefly, the space above the phosphorus pentabromide is full of dry air, which is kept at constant volume throughout the experiment by a thread of mercury contained in a graduated U-tube of 2 mm. bore. The other limb of this communicates through a closed space full of air with a manometer open to the air on the further side, and furnished with a mercury reservoir which can be raised and lowered ; thus at the same time regulating and registering the pressures.

In these circumstances it can be shown that the pressures recorded are simply the vapour pressures of the substance. No correction need be introduced for the increase of pressure on heating the enclosed air, provided this is less than the vapour pressure in question.

The method was checked by a determination of the vapour pressures of benzene ; these were found to agree with the values determined by Regnault and Ramsay within 4 cm. of mercury at 50° and within 1 cm. at 78°.

The vapour pressures of phosphorus pentabromide were then measured, and it is believed that they can be relied on certainly within 5 cm. of mercury, that is, the boiling point as deduced from the vapour pressures is within 2° of the true value.

Temp.	Vapour pressure in cm. of mercury.
23°	0·6
41	3·5
61	10·9
62	12·0
75°	21·7
79	23·7
88	31·8 and 35·6
100	56·0

From these results by extrapolation the temperature at which the vapour pressure of liquid phosphorus pentabromide is 76 cm. is estimated to be 106° ± 2°.

Comparison Temperatures.—Practically, in the case of substances of which the vapour pressures and liquid volumes below the boiling point are known, it will be shown later that any temperatures at which the vapour pressures are equal may be chosen as comparison temperatures within a considerable range.

Theoretically, also, the differences between the atomic volumes of different liquids at temperatures of equal vapour pressure would be constant, provided the critical pressures were equal. As a matter of fact the critical pressures of the liquids in question are mostly unknown and probably different ; yet the difference between volumes at temperatures of equal vapour pressures is, indeed, so constant that the relations stated for the boiling point will also hold for temperatures 40° removed from it. A few figures will make this clear.

Table I gives the temperatures and atomic volumes corresponding with the three pressures : (1) 760 mm., (2) 200 mm., (3) 100 mm. These have been calculated from the data of the investigators into volumes and vapour pressures of chlorine, bromine, and phosphorus.

Table II gives temperatures and molecular volumes at these pressures for PCl_3, PBr_5, P + 3Cl, and P + 5Br, the two last being taken from the values in table I; thus, *V*(P + 3Cl) at 200 mm. is the atomic volume of phosphorus measured at a vapour pressure of 200 mm. plus three times the atomic volume of chlorine measured at a vapour pressure of 200 mm.

Table III gives the differences of volume at the temperatures corresponding with these vapour pressures.

TABLE I

P.	Cl.		Br.		P.	
Mm.	*T°.*	*V.*	*T°.*	*V.*	*T°.*	*V.*
760	−33·6°	22·76	+59°	26·8	+290°	20·4
200	61	21·8	23·5	25·6	179	19·1
100	73	21·5	8·2	25·4	163	19·0

TABLE II.

P.	PCl_3.		P + 3Cl.	PBr_5.		P + 5Br.
Mm.	*T°.*	*V.*	*V.*	*T°.*	*V.*	
760	76°	93·34	88·68	106° *	157·3	154·4
200	36	89·0	84·5	76	149·6	147·1
100	20	87·3	83·5	—	—	—

* By extrapolation.

TABLE III.

P (mm.).	Br − Cl.	Br − P.	PCl_3 − (P + 3Cl).	PBr_5 − (P + 5Br.)
760	4·0	6·4	4·7	2·9
200	3·8	6·5	4·5	2·5
100	3·9	6·4	3·8	—

Of the four other phosphorus halides, namely, phosphorus tribromide, phosphorus pentachloride, phosphoryl chloride, and phosphoryl dichlorobromide, the specific volumes of which are accurately known, the vapour pressures have not yet been determined. The volumes at the boiling points are known, and there is little doubt that the differences of molecular volume would remain much the same for a considerable range of temperature.

Comparing as before the sum of atomic volumes of the free elements, the value 14·1 is put for oxygen instead of one of Kopp's numbers. This value is the mean of the closely concordant values found by Dewar (*Proc. Roy. Soc.*, 1893, **15**, 133), and Drugman and Ramsay (Trans., 1900, **77**, 1228), by different methods for the atomic volumes of liquid oxygen at its boiling point.

TABLE IV.

I.	II. Mol. vol. of compound.	III. Sum of at. vols. of elements.	IV. Expansion column II. minus column III.	V. At. vol. of phosphorus if other elements retain their at. vol. in combination.
PCl_3	93·34	88·68	+4·7	25·1
PBr_3	108·8	100·8	+8·0	28·4
PCl_5	128·9	134·2	−5·3	15·1
PBr_5	157·3	154·4	+2·9	23·3
$POCl_3$	101·3	102·8	−1·5	18·9
$POBrCl_2$	107·4	106·8	+0·6	21·0

That expansion on combination is greater in the case of a bromine compound than in the corresponding chlorine compound may be seen on comparing phosphorus tribromide with phosphorus trichloride, etc. In the case of phosphorus pentachloride and phosphoryl chloride the molecular volumes are less than the sums of the atomic volumes.

Or, taking the figures of column V, it is evident that the atomic volume of phosphorus combined with bromine is greater than that of phosphorus combined with chlorine.

If, on the other hand, we compare with one another compounds in which phosphorus exhibits different valencies towards the same halogen, we see that the expansion on combination is greater in the case of the tri- than in that of the penta-compound.

Or, taking the figures of column V, it is evident that the atomic volumes of tervalent phosphorus are throughout these compounds greater than those of quinquevalent phosphorus.

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LVI.—*The Action of Ethyl Carbamate on Esters of Organic Acids and Mustard Oils.*

By SIEGFRIED RUHEMANN and JOHN GILLIES PRIESTLEY.

IN continuation of the research on the esters of acetylenic acids, we have subjected the sodium derivative of ethyl carbamate to the action of ethyl phenylpropiolate with the view of ascertaining whether in this case, also, a union is effected as represented by the equation:

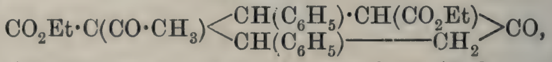
$$C_6H_5{\cdot}C{\vdots}C{\cdot}CO_2Et + NHNa{\cdot}CO_2Et = C_6H_5{\cdot}C(NH{\cdot}CO_2Et){:}CNa{\cdot}CO_2Et.$$

We find, however, that such an additive product is not formed, but instead, alcohol is eliminated, and ethyl phenylpropiolylcarbamate, $C_6H_5\cdot C\vdots C\cdot CO\cdot NH\cdot CO_2Et$, is produced.

Some time ago, Hantzsch (*Ber.*, 1894, **27**, 1250) showed that, in the presence of sodium ethoxide, ethyl carbamate does not condense with esters of fatty acids to yield acyl derivatives of ethyl carbamate, the only exception being ethyl oxalate, which yields diethyl oxalyldicarbamate, $(CO\cdot NH\cdot CO_2Et)_2$. The acyl derivatives of ethyl carbamate had to be prepared by the action of acid chlorides or acid anhydrides on ethyl carbamate. Those compounds may, however, be obtained also in a manner similar to the formation of ethyl phenylpropiolylcarbamate by the action of ethyl sodiocarbamate on the esters of fatty or fatty-aromatic acids. This reaction, moreover, allows of the preparation of ethyl formylcarbamate, which, on account of the non-existence of formyl chloride, cannot be produced by the old method. Owing to the fact that ethyl formylcarbamate is readily hydrolysed, a mixture of this substance and ethyl carbamate, which melts at a low temperature, is produced in the reaction. On being kept for several days in a desiccator, the oil deposits a small quantity only of the formyl compound, and, as a complete separation cannot be effected by fractional distillation in a vacuum, the yield of the pure ethyl formylcarbamate is rather small.

On applying this reaction to the esters of benzenecarboxylic acids, it has been found that ethyl benzoate forms only a small quantity of ethyl benzoylcarbamate, whereas ethyl *o*-phthalate does not yield a trace of the carbamate.

Of interest is the behaviour of ethyl sodiocarbamate towards ethyl benzylideneacetoacetate. This reaction furnishes diethyl acetyldiphenyl*cyclo*hexanonedicarboxylate,



$$CO_2Et\cdot C(CO\cdot CH_3)<\begin{matrix} CH(C_6H_5)\cdot CH(CO_2Et) \\ CH(C_6H_5)\text{————}CH_2 \end{matrix}>CO,$$

identical with the compound which one of us (Ruhemann, Trans., 1909, **95**, 110) obtained by the action of sodium phenoxide or sodium ethoxide on ethyl benzylideneacetoacetate.

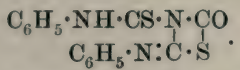
In connexion with this work, we have studied the behaviour of ethyl sodiocarbamate towards mustard oils. On using phenylthiocarbimides, the reaction takes place in two phases. At first, both substances unite to form carboxyethylphenylthiocarbimide,

$$CO_2Et\cdot NH\cdot CS\cdot NH\cdot C_6H_5,$$

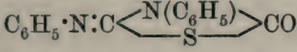
which, indeed, could be isolated and identified with the product obtained by Doran (Trans., 1896, **69**, 326) on treatment of carboxyethylthiocyanide with aniline. The yield of this substance from ethyl carbamate is very small, as the greater part of it subsequently condenses with another molecule of phenylthiocarbimide, thus :

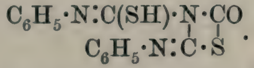
$$CO_2Et\cdot NH\cdot CS\cdot NH\cdot C_6H_5 + C_6H_5\cdot NCS = C_{15}H_{11}ON_3S_2 + C_2H_6O,$$

and yields a compound the constitution of which is to be represented by the formula



$$\begin{array}{l} C_6H_5\cdot NH\cdot CS\cdot \underset{|}{N}\cdot \underset{|}{C}O \\ \qquad\quad C_6H_5\cdot N{:}C\cdot S \end{array}.$$

This substance, which stands in a close relationship to carbonylthiocarbanilide,  $C_6H_5\cdot N{:}C{<}\begin{matrix}N(C_6H_5)\\ S\end{matrix}{>}CO$, the product of the action of carbonyl chloride on thiocarbanilide, is, therefore, to be regarded as *anhydrodiphenyldithiobiuretcarboxylic acid.* The compound is yellow, whereas its sodium and potassium derivatives are colourless. This fact leads to the view that the salts are derived from the tautomeric formula



$$\begin{array}{l} C_6H_5\cdot N{:}C(SH)\cdot \underset{|}{N}\cdot \underset{|}{C}O \\ \qquad\qquad C_6H_5\cdot N{:}C\cdot S \end{array}.$$

The yellow substance is scarcely attacked on boiling with hydrochloric acid, but it is very sensitive towards potassium hydroxide. The colourless salt, which is first formed on the addition of the dilute alkali, decomposes when digested on the water-bath for a short time.

Analogous to the behaviour of phenylthiocarbimide is the action of ethyl sodiocarbamate on allylthiocarbimide, whereby *anhydrodiallyldithiobiuretcarboxylic acid,* $C_9H_{11}ON_3S_2$, is produced.

EXPERIMENTAL.

Ethyl Phenylpropiolylcarbamate, $C_6H_5\cdot C{:}C\cdot CO\cdot NH\cdot CO_2Et$.

This compound is formed by digesting a solution of ethyl carbamate (4·5 grams) in absolute ether with sodium wire (1·2 grams) on the water-bath until the metal has disappeared, then adding ethyl phenylpropiolate (8·7 grams) to the voluminous mass of ethyl sodiocarbamate, and keeping the mixture for a day or warming it on the water-bath for one to two hours. On pouring the whole into water, removing the ethereal layer (which contains only traces of ethyl carbamate and ethyl phenylpropiolate), and treating the aqueous solution with an excess of dilute sulphuric acid, an emulsion is produced. This, in a short time, deposits a solid, which is very soluble in alcohol, especially on boiling, and crystallises from dilute alcohol in colourless prisms melting at 100°:

0·2070 gave 0·5030 CO_2 and 0·0965 H_2O. $C = 66·27$; $H = 5·17$.
0·2560 „ 14·6 c.c. N_2 at 18° and 752 mm. $N = 6·51$.
$C_{12}H_{11}O_3N$ requires $C = 66·35$; $H = 5·07$; $N = 6·45$ per cent.

Ethyl phenylpropiolylcarbamate, on being in contact with concentrated aqueous ammonia for a few hours, dissolves, and, in the course of a day, the solution sets to a semi-solid mass of crystals. These readily dissolve in boiling water, and, on cooling, crystallise in colourless prisms. The compound is phenylpropiolamide,

$$C_6H_5\cdot C\vdots C\cdot CO\cdot NH_2,$$

which Stockhausen and Gattermann (*Ber.*, 1892, **25**, 3537) obtained by the action of ammonium carbonate on phenylpropiolyl chloride. They gave the melting point as 99—100°, whereas we find it to be 108—109°:

0·2060 gave 0·5620 CO_2 and 0·0928 H_2O. C = 74·40; H = 5·0.
0·2158 ,, 18 c.c. N_2 at 15° and 764 mm. N = 9·82.
C_9H_7ON requires C = 74·48; H = 4·83; N = 9·65 per cent.

Ethyl Phenylacetylcarbamate, $C_6H_5\cdot CH_2\cdot CO\cdot NH\cdot CO_2Et$.

It has been mentioned in the introduction to this paper that ethyl benzoate, on treatment with ethyl sodiocarbamate, yields only a very small quantity of ethyl benzoylcarbamate, and that no trace of an acylcarbamate is formed from ethyl *o*-phthalate. This result is probably due to steric hindrance, for, as shown before, ethyl phenylpropiolate readily reacts with ethyl sodiocarbamate, and gives a good yield of the acylcarbamate. Ethyl phenylacetate (16·4 grams) also condenses with ethyl sodiocarbamate (produced from 9 grams of ethyl carbamate and 2·3 grams of sodium in absolute ether). The mixture, after being kept for two days, is poured into water, the ethereal layer separated from the aqueous solution, and the latter treated with dilute hydrochloric acid, when a solid is precipitated. This is readily soluble in alcohol, and crystallises from dilute alcohol in colourless, silky needles melting at 114—115°:

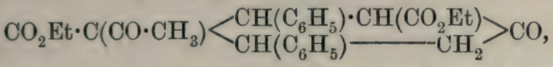
0·2075 gave 0·4845 CO_2 and 0·1175 H_2O. C = 63·68; H = 6·29.
0·2255 ,, 13·2 c.c. N_2 at 14° and 767 mm. N = 6·94.
$C_{11}H_{13}O_3N$ requires C = 63·76; H = 6·28; N = 6·76 per cent.

This compound, also, is hydrolysed by ammonia, and yields phenylacetamide in addition to phenylacetic acid. The former separates on leaving the carbamate in contact with concentrated aqueous ammonia for several days, and crystallises from boiling water in colourless plates. It was identified by the melting point (154—155°) and a nitrogen estimation:

0·1474 gave 13·6 c.c. N_2 at 24° and 772 mm. N = 10·5.
C_8H_9ON requires N = 10·37 per cent.

Action of Ethyl Sodiocarbamate on Ethyl Benzylideneacetoacetate.

On adding to ethyl sodiocarbamate (from 2·3 grams of sodium and 9 grams of ethylcarbamate), suspended in absolute ether, ethyl benzylideneacetoacetate (21·8 grams), heat is developed, the ethyl sodiocarbamate disappears, and a yellow solid separates. After being kept overnight, the whole is poured into water. The aqueous solution contains only a small quantity of a viscous product; the ethereal layer, on evaporation of the ether, yields an oil which, when stirred with a little alcohol, partly solidifies. The product is filtered with the aid of the pump, and washed with alcohol until the filtrate ceases to be yellow. The solid is free from nitrogen, and, after crystallisation from alcohol, has the same melting point and chemical behaviour as diethyl 6-acetyl-1 : 5-diphenyl*cyclo*hexan-3-one-2 : 6-dicarboxylate,



$$\mathrm{CO_2Et\cdot C(CO\cdot CH_3)}<\begin{matrix}\mathrm{CH(C_6H_5)\cdot CH(CO_2Et)}\\ \mathrm{CH(C_6H_5)}\text{———}\mathrm{CH_2}\end{matrix}>\mathrm{CO},$$

which has recently been described by one of us (*loc. cit.*). The formula, moreover, was verified by analysis:

0·2122 gave 0·5565 CO_2 and 0·1240 H_2O. C = 71·52; H = 6·49.

$C_{26}H_{28}O_6$ requires C = 71·56; H = 6·42 per cent.

The alcoholic washings from the compound contain a yellow, viscous product, from which no crystalline substance could be extracted.

Diethyl Oxalyldicarbamate, $(CO\cdot NH\cdot CO_2Et)_2$.

This compound, which Hantzsch (*loc. cit.*) obtained by the action of an alcoholic solution of sodium ethoxide on a mixture of ethyl carbamate and ethyl oxalate, is formed, also, by dissolving sodium (2·3 grams) in a solution of ethyl carbamate (9 grams) in absolute ether, then adding ethyl oxalate (7·5 grams), and digesting the mixture on the water-bath for two to three hours. The product is poured into water, and the aqueous layer treated with dilute hydrochloric acid, when a solid is precipitated. This is almost insoluble in cold water, but readily dissolves in boiling water, and, on cooling, separates in colourless, stout prisms, which melt at the same temperature (170°) as observed by Hantzsch:

0·2054 gave 0·3115 CO_2 and 0·0980 H_2O. C = 41·36; H = 5·30.

0·2265 ,, 23·2 c.c. N_2 at 15° and 777 mm. N = 12·27.

$C_8H_{12}O_6N_2$ requires C = 41·38; H = 5·17; N = 12·07 per cent.

This substance, on hydrolysis with concentrated aqueous ammonia, yields oxamide.

Ethyl Chloroacetylcarbamate, $CH_2Cl\cdot CO\cdot NH\cdot CO_2Et$.

Frerichs (*Arch. Pharm.*, 1899, **237**, 288) prepared this compound from chloroacetyl chloride and ethyl carbamate. We obtained it by digesting the mixture of ethyl sodiocarbamate (from 2·3 grams of sodium and 9 grams of ethyl carbamate), suspended in absolute ether, and ethyl chloroacetate (12·3 grams) on the water-bath for two hours. The whole is then poured into water, and the aqueous solution, after treatment with dilute sulphuric acid, frequently extracted with ether. On evaporation of the ether, a solid is left, which is sparingly soluble in ether but dissolves readily in boiling water, and, on cooling, crystallises in colourless prisms melting at 129—130°:

0·2154 gave 15·8 c.c. N_2 at 18° and 764 mm. N = 8·49.
$C_5H_8O_3NCl$ requires N = 8·46 per cent.

Ethyl Formylcarbamate, $CHO\cdot NH\cdot CO_2Et$.

On adding freshly distilled ethyl formate (8 grams) to ethyl sodiocarbamate (prepared by dissolving 2·3 grams of sodium in a solution of 9 grams of ethyl carbamate in absolute ether) and frequently shaking the mixture, the powdery ethyl sodiocarbamate is transformed into a white solid, which adheres to the sides of the vessel. The mixture, after being kept overnight, is poured into water, when the whole dissolves. The ethereal layer, which contains only a small quantity of ethyl carbamate, is removed from the aqueous solution, the latter treated with dilute sulphuric acid, and extracted ten times with ether. On evaporation of the ether, an oil is left from which, in the course of three to four days, a crystalline solid separates. This is collected with the aid of the pump, and the adhering oil pressed off between filter paper. The substance is very soluble in ether, but almost insoluble in light petroleum, and crystallises from a mixture of both solvents in colourless prisms, which are rather volatile in a vacuum, even at the ordinary temperature, and melt at 51—52°:

0·1994 gave 0·3007 CO_2 and 0·1097 H_2O. C = 41·12; H = 6·11.
0·1800 „ 18·4 c.c. N_2 at 17° and 774 mm. N = 12·06.
$C_4H_7O_3N$ requires C = 41·02; H = 5·96; N = 11·97 per cent.

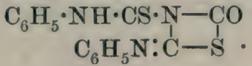
Although almost the total quantity of ethyl sodiocarbamate reacts with ethyl formate, as indicated by the fact that the ethereal solution after treatment of the product with water contains only a little ethyl carbamate, yet the yield of ethyl formylcarbamate is rather small. This circumstance is partly due to the volatility of the compound, especially, however, to the ease with which it is hydrolysed by mineral acids, even in the cold. The oil which is left on evaporation of the ether from the ethereal extract of the acidified aqueous solution of the product of the reaction, is a mixture of ethyl carbamate and its formyl derivative. This melts at a low temperature; it distils at 73—82°/13 mm., and cannot be completely separated by fractional distillation. A nitrogen estimation of the fraction which boils at 73—77°/13 mm. and melts at 35—39° gave the following result:

0·1639 gave 21·4 c.c. N_2 at 19° and 776 mm. N = 15·29.
Ethyl carbamate requires N = 15·73 per cent.
Ethyl formylcarbamate requires N = 11·97 per cent.

This indicates that the fraction is a mixture of about 88 per cent. ethyl carbamate and 12 per cent. ethyl formylcarbamate. The higher boiling fraction of the oil contains a larger percentage of the formyl derivative; on cooling, it solidifies, and the solid, after removal of the easily fusible portion by pressing between filter paper and crystallisation from a mixture of ether and light petroleum, yields a further quantity of the formyl compound.

Action of Ethyl Sodiocarbamate on Mustard Oils.

Anhydrodiphenyldithiobiuretcarboxylic Acid,



$$\begin{array}{l} C_6H_5\cdot NH\cdot CS\cdot N - CO \\ \qquad\quad\;\; | \qquad\; | \\ \qquad C_6H_5N{:}C - S \end{array} .$$

Phenylthiocarbimide (13·5 grams) reacts with ethyl sodiocarbamate (obtained by dissolving 2·3 grams of sodium in a solution of 9 grams of ethyl carbamate in absolute ether) on keeping the mixture at the ordinary temperature for two days. The product of the reaction is poured into water, and the aqueous solution separated from the ethereal layer. The latter contains ethyl carbamate besides traces of phenylthiocarbimide. The aqueous solution, when treated with dilute sulphuric acid, yields a yellow solid, which is a mixture of carboxyethylphenylthiocarbimide, $CO_2Et\cdot NH\cdot CS\cdot NH\cdot C_6H_5$, and anhydrodiphenyldithiobiuretcarboxylic acid, $C_{15}H_{11}ON_3S_2$; their separation is effected by shaking the ethereal solution of the mixture with sodium carbonate, which extracts the thiobiuret derivative. On evaporating the ethereal layer, a solid (3 grams) is left, which crystallises from dilute alcohol in colourless plates melting at 130°:

0·1432 gave 15·8 c.c. N_2 at 20° and 760 mm. N = 12·62.
$C_{10}H_{12}O_2N_2S$ requires N = 12·50 per cent.

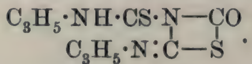
This substance is identical with the compound which Doran (*loc. cit.*) obtained by the action of aniline on carboxyethylthiocarbimide, $CNS\cdot CO_2Et$.

On adding dilute hydrochloric acid to the sodium carbonate solution of the mixture, a yellow solid (8 grams) is precipitated, which is readily soluble in ether or chloroform, sparingly, so in cold, but readily so in boiling, alcohol, and, on cooling, crystallises in yellow prisms. These soften at 232° and melt and evolve gas at 234—235°:

0·1802 gave 0·3794 CO_2 and 0·0590 H_2O. C = 57·42; H = 3·63.
0·2115 „ 24·4 c.c. N_2 at 18° and 775 mm. N = 13·58.
0·2053 „ 0·3060 $BaSO_4$. S = 20·46.
$C_{15}H_{11}ON_3S_2$ requires C = 57·51; H = 3·51; N = 13·42; S = 20·44 per cent.

The compound is scarcely attacked by dilute hydrochloric acid. It dissolves in dilute sodium carbonate to yield a colourless solution, from which the yellow substance is precipitated on the addition of mineral acids. This behaviour is due to the formation of a colourless salt, which is produced, also, on adding dilute sodium hydroxide to the yellow solid. Complete decomposition, however, takes place if the substance is digested with the dilute alkali for half an hour on the water-bath. Phenylthiocarbimide, aniline, thiocarbanilide, carbon dioxide, and hydrogen sulphide were identified as the products which are formed. The compound $C_{15}H_{11}ON_3S_2$ is readily soluble in dilute ammonia, yielding a colourless solution which gives silver sulphide on the addition of silver nitrate.

Anhydrodiallyldithiobiuretcarboxylic acid,



$$\begin{array}{l} C_3H_5\cdot NH\cdot CS\cdot N—CO \\ \qquad\quad C_3H_5\cdot N:C—S \end{array}.$$

This compound is prepared in the same way as the former by keeping the mixture of allylthiocarbimide and ethyl sodiocarbamate suspended in absolute ether for two days. On proceeding as in the previous case, a small quantity of a colourless substance was obtained, which is insoluble in sodium carbonate. This has not been further examined, but there can be no doubt that it is carboxyethylallylthiocarbimide, $C_3H_5\cdot NH\cdot CS\cdot NH\cdot CO_2Et$. The solution of the product of the reaction in sodium carbonate, on the addition of dilute hydrochloric acid, yields a yellow precipitate, which is readily soluble in ether or alcohol, and crystallises from dilute alcohol in pale yellow prisms; these soften at 129° and melt at 132—133°:

0·1933 gave 29·6 c.c. N_2 at 22° and 770 mm. N = 17·57.

$C_9H_{11}ON_3S_2$ requires N = 17·43 per cent.

This substance resembles in its behaviour the corresponding compound from phenylthiocarbimide; like the former, it dissolves in sodium carbonate to yield a colourless solution.

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LVII.—*Analytical Investigation of Zirconium Metal.*

By E. WEDEKIND, Ph.D., and S. JUDD LEWIS, B.Sc., F.I.C.

ELEMENTARY zirconium is not yet known in a pure condition. Berzelius was the first to prepare the amorphous modification by the action of potassium on zirconium potassium fluoride, K_2ZrF_6, but he made no statement whatever relative to the composition of the products he obtained. Later T. L. Phipson (*Compt. rend.*, 1865, **61**, 745), Clemens Winkler (*Ber.*, 1890, **23**, 2664; 1891, **24**, 888), as well as Dennis and Spencer (*J. Amer. Chem. Soc.*, 1896, **18**, 673), have attempted to prepare zirconium by reduction of the dioxide with magnesium; Phipson again communicates no analytical data concerning the degree of purity of his zirconium, whilst Dennis and Spencer pronounce their product of reduction to be zirconium monoxide mixed with a little elementary zirconium.

Winkler's product contained about 80·7 per cent. of zirconium, and was essentially a mixture of zirconium hydride (ZrH_2) and unchanged dioxide. Concerning crystallised zirconium, we have the reports of Troost (*Compt. rend.*, 1865, **61**, 109), Franz (*Ber.*, 1870, **3**, 58), and Moissan (*Compt. rend.*, 1893, **116**, 1122), but even here the analytical examinations have not been altogether satisfactory, for the so-called crystallised zirconium of Troost has been shown to be an aluminium zirconide, $ZrAl_2$ (E. Wedekind, *Zeitsch. Elektrochem.*, 1904, **10**, 331), and the product obtained by Troost (*Compt. rend.*, 1893, **116**, 1227) and Moissan by reduction of zirconium dioxide with carbon must have contained carbon or a carbide, since it was prepared in an electric-arc furnace with carbon electrodes.

From this brief review, it is clear that the first condition for further investigation on the preparation of pure zirconium is to find suitable methods whereby one can ascertain accurately the quantitative composition of the products obtained by the various processes of reduction. Only in this way will it be possible to guard against disturbing impurities in fresh attempts to obtain the metal. We have recently shown (E. Wedekind, in conjunction with S. Judd Lewis, *Zeitsch. Chem. Ind. Kolloide*, 1908, **2**, 289) that the amorphous zirconium prepared by the Berzelius process contains only 36 per cent. of the *free* element, and that this value can be doubled by suitable precautionary measures. For the determination of the combined and uncombined zirconium, we have devised a special method, which serves also as a means of ascertaining directly the proportion of oxygen. Further, we have worked out methods for the determination of nitrogen and carbon which are described below; also, reference is made to our experience with the drying of amorphous zirconium.

Methods of Analysis.

Oxygen.—Amongst our earlier investigations of the various forms of metallic zirconium, several determinations of the element were made, but always with a considerable difference from 100 per cent. With the amorphous variety, 15 or 16 per cent. had to be accounted for, and in this we confirmed the observations of some other workers. By evaporating the colloidal solution, and still better by using the spontaneously precipitated colloid from a pure solution, we hoped for greater purity of the element, but the only satisfaction gained was an approximate constancy of the deficiency. With the impure metal after fusion there was no regularity of oxygen content, and it became very unsatisfactory to attribute the deficiency to oxygen without some positive evidence. In order to determine the oxygen directly, the metal was heated in dry chlorine free from oxygen and all other gases, as even carbon dioxide is decomposed by zirconium at higher temperatures, and nitrogen is absorbed by it with formation of the nitride.

By this means, the free zirconium was converted into the volatile tetrachloride, $ZrCl_4$, whilst the oxygen and the zirconium existing in combination therewith were left behind as zirconium dioxide.

At first, some difficulty was experienced in obtaining a continuous stream of sufficiently pure chlorine, and in avoiding at the same time any possible entrance of air into the apparatus; Fig. I shows the arrangement finally adopted. In order to be sure that the zirconium itself (about 0·5 gram accurately weighed in the boat, *A*) and the combustion tube are quite free from moisture, it is desirable to heat them for a few minutes in a current of pure hydrogen, freedom from oxygen being further assured by passing the gas through alkaline pyrogallol (*B*) and sulphuric acid (*C*). In order to free the apparatus from air, the hydrogen was passed for an hour before applying heat, the gas escaping by the exit (*D*), the cock (*E*) being closed.

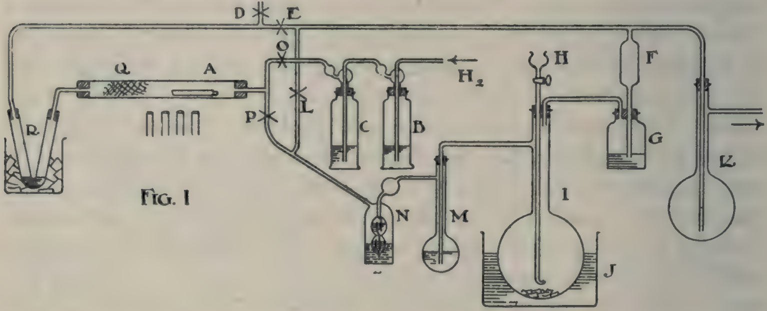

FIG. I

Meanwhile the pipette (*F*) is raised above the surface of the concentrated sulphuric acid contained in the trap (*G*), and pure concentrated hydrochloric acid is allowed to drop from the funnel (*H*) on to pure potassium permanganate crystals contained in the flask (*I*), which is cooled by water in the bath (*J*).

Chlorine is generated, and the flow can be regulated by adjusting the supply of acid. If necessary, at a later stage, when the permanganate is exhausted, the flask may be warmed, and more chlorine will be evolved; but it is better to start with sufficient permanganate to avoid this; 15 grams per hour is a safe allowance. The gas is allowed to escape for half an hour through (*G*, *F*) and the reservoir flask (*K*) into the open air. The object of the flask (*K*) is to provide an atmosphere of pure chlorine in the event of any irregularity in the supply of chlorine, or of a too rapid absorption of chlorine by the zirconium. The pipette (*F*) is then lowered, the cock (*L*) is opened, and for another half-hour the gas escapes through the apparatus (*M*) and (*N*), containing concentrated sulphuric acid. By this time, the whole apparatus, which is of small capacity, may be considered to be free from air. Blank tests with hydrogen, not purified by pyrogallol, showed that all air is removed in less than half the above time; also, experiments carried out with tin in place of zirconium, under conditions identical with those now described, proved absolute freedom from air.

The question of the purity of chlorine generated from potassium permanganate and concentrated hydrochloric acid was considered, and has been fully dealt with (Proc., 1909, **25**, 59). The only reason for preferring the permanganate method is that a regular stream of chlorine can be maintained for a long time, whereas with pure manganese dioxide it is much more difficult to control the flow and to maintain it sufficiently constant for the necessary time. After cooling in hydrogen, if desired, the boat can be re-weighed to ascertain the proportion of moisture, the hydrogen being continuously passed until one wishes to employ the chlorine. The tube must be quite cold before passing the chlorine, as otherwise explosion with the residual hydrogen may occur.* The cocks (*L*) and (*O*) are then closed, and (*P*) is opened. After a few minutes, (*D*) is closed, (*E*) opened, and the boat gently heated. Very soon the zirconium burns brightly in the chlorine, and a dense sublimate of zirconium tetrachloride, $ZrCl_4$, is deposited in the tube.

The progress of the reaction is regulated as much as possible by the application of heat. By increasing the heat, the sublimate is driven forward to the cool part of the tube at (*Q*), whilst finally the boat is maintained for some time at the full temperature of the furnace in order to volatilise all tetrachloride. The V-tube (*R*), containing 10 per cent. hydrochloric acid and surrounded by ice, acts as a trap for escaping vapour of the tetrachloride.†

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* This happened on two occasions when working with amorphous zirconium; in the first instance the temperature of the tube was judged to be about 60°, and in the second not more than about 40°.

† The low temperature and the presence of the acid prevent any sensible quantity

When cold, the boat containing the oxygen as zirconium dioxide is weighed, and the proportions of oxygen and oxidised zirconium are calculated. The tetrachloride is washed out of the combustion tube and the trap (*R*), precipitated by ammonia, and weighed as dioxide, whence the zirconium existing in the free state in the impure metal can be determined. This simple method does not always give sufficiently accurate results, because occasionally a little oxide is thrown out of the boat on account of the vigour of the reaction, and also because the oxide in the boat sometimes contains a little chloride and loses weight on heating strongly. It is, therefore, usually necessary to filter the solution of zirconium oxychloride (formed by interaction of the tetrachloride with water) through an ashless filter, wash, throw the oxide in the boat on to the same filter and wash thoroughly, then to determine the zirconium in the two parts as before.

Zirconium.—From simple solutions of zirconium salts, the zirconium can be completely precipitated by ammonia, provided a large excess of the reagent and a little ammonium chloride be employed; the latter assists the precipitate to form and to filter more quickly. With dilute ammonia and the fixed alkalis, the separation is not always complete. To the solution, half its volume of the strongest solution of ammonia and one per cent. of ammonium chloride are added, then the liquid is warmed and set aside for two or three hours or overnight. In 300 c.c. of the filtrate, from which 0·6 gram of zirconium dioxide had separated, the loss was less than 0·0001 gram.

Drying, etc.—Instead of drying the amorphous and colloidal substances in hydrogen, as described above, one can with advantage use the following simple apparatus and dry in a vacuum. A boat containing a known weight of the substance is placed in a horizontal Jena glass test-tube into which is fitted a stopcock connected with a good pump. This test-tube and a thermometer are fixed through a cork into a larger test-tube sheathed in asbestos paper, and placed on the top of the tiles of a combustion furnace. A temperature of 200°, or nearly that, is necessary for complete dehydration. The apparatus works well within the limits of the mercurial thermometer, and, by using a three-way cock, various gases and vapours may be introduced into the reaction tube, and their influence on zirconium at known temperatures watched with convenience.

Nitrogen.—The sum of the zirconium and oxygen did not usually

of water vapour being drawn into the combustion tube in the event of the pressure diminishing, due to a too rapid absorption of the gas. This, however, rarely happens, and never to any significant degree.

account for all, and then it was found that considerable quantities of nitrogen were also present, whilst occasionally other elements were found. The presence of nitrogen is very readily ascertained by heating a little of the metal with moistened solid alkali hydroxide perfectly free from nitrogen in any form, and testing the vapour evolved for ammonia. Unfortunately, nearly all samples of alkali contain nitrates or nitrogen in some other form, except those of sodium hydroxide prepared from sodium; hence it is generally more practical to heat a few milligrams of the powdered zirconium in concentrated sulphuric acid for five minutes, and, when cold, to dilute and warm with excess of alkali, testing the vapour given off for ammonia.

For quantitative work, the finely powdered zirconium is placed in a flask, and a few c.c. of concentrated sulphuric acid are added. The mixture is heated cautiously, as the reaction may suddenly become somewhat violent. When all the metal is combined and the nitrogen converted into ammonia, water and alkali are added, and the ammonia distilled into a known quantity of standard acid in the usual way. There is sometimes considerable difficulty in completing the reaction; indeed, it may not be finished after two or three days' heating. A much more convenient method is to dissolve the substance in a mixture of sulphuric and hydrofluoric acids and distil this solution with alkali as before.

Carbon.—In view of combined carbon having entered into the mixture from which specimen "*B*" was prepared, it became necessary to ascertain the quantity of this element should it be present. As zirconium and carbon burn so readily and completely in oxygen, and as their oxides are so easily separated, a method of ordinary combustion appeared to be the most suitable, provided the extreme violence of the combustion of the metal in oxygen could be moderated sufficiently. Finally, the following method was devised, and found to work with constancy and accuracy. The zirconium was heated in a vacuum in a combustion tube, and oxygen introduced so gradually as to allow the metal to burn quite quietly. Fig. II shows the apparatus employed.

Pure oxygen, as for an ordinary combustion, is supplied through the cock (*b*) and made to fill the tube, then the cocks (*b*) and (*c*) are closed, and the whole apparatus between these points is thoroughly exhausted by means of the pump, the three-way cock (*a*) being repeatedly turned. The pump is now shut off, and the cock (*a*) left open to the apparatus in both directions. Then the copper spiral (*d*) is heated, and also the zirconium (*very finely* powdered) in the boat (*e*). The latter should be heated sufficiently to cause it to ignite readily in oxygen at a low pressure. Very cautiously the oxygen is allowed to enter—five or six bubbles at a time. When about fifteen or twenty bubbles have passed, the zirconium begins to glow, although the capacity of the apparatus between the cocks (*b*) and (*c*) is about 300 c.c. A very slow, regular current of oxygen may now be started, and the rate increased as the reaction moderates, until the pressure of the oxygen is equal to that of the atmosphere. Two or three drops of sulphuric acid in the tube (*f*) serve to indicate the direction of the pressure on cautiously turning the cock (*c*). While the oxygen is at atmospheric pressure the tube is heated to full redness for fifteen minutes. The combustion takes about one hour. The 200 c.c. separator (*g*) is introduced to increase the capacity of the apparatus, thus keeping the pressure of oxygen under better control, and to draw over more oxygen. The furnace is now stopped, purified air is supplied instead of oxygen, the cocks (*b*) and (*c*) are opened, and about a litre of air is slowly drawn through the apparatus by means of the aspirator; finally, the potash bulbs (*h*) are weighed, and the weight of carbon dioxide ascertained. The tube (*i*) contains pumice stone moistened with sulphuric acid, as for an ordinary combustion.

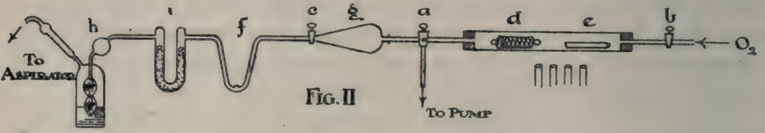

FIG. II

This should be unnecessary; but, in view of the very small quantity of carbon to be determined, it is imperative to secure the removal of the least trace of moisture from the gas. The copper spiral is probably not required, but, as a precaution, it was introduced to decompose any oxides of nitrogen which might be formed from the oxygen gas and the nitrogen combined with the metal.

From 0·3954 gram of metal, 0·0013 gram of carbon dioxide was produced, equivalent to 0·089 per cent. of carbon. From 0·5197 gram of another piece of the same sample of metal, 0·0015 gram of carbon dioxide was obtained, equivalent to 0·079 per cent. of carbon. In one blank experiment, the potash bulbs lost 0·0002 gram, and in another, they gained 0·0001 gram.

During the combustion of the zirconium, although the pressure of oxygen was so small, the metal burnt along the boat very gradually, so that the portion at the front was scarcely altered in appearance when that at the back and in the middle of the boat was already burnt. The contents of the boat increased enormously in bulk and swelled up in cloud-like rolls.

At first, trials were made with absorption tubes containing solid potassium hydroxide or soda-lime in the vacuum system, but this arrangement was useless, because the absorbent lost greatly in weight under these conditions.

Hydrogen.—The apparatus shown in Fig. II, omitting the tube (*f*), has also been used for the determination of water, and hydrogen in other forms, in amorphous zirconium with approximately satisfactory results. Two examinations of the same sample gave the following results: 0·1742 gram of amorphous zirconium was dried in a vacuum in the manner described above, and then a combustion of the dried substance by the carbon method was made. 0·0072 gram (=4·133 per cent.) of water was found in the drying, and 0·0035 gram of water (=0·239 per cent. of hydrogen) in the combustion. 0·1918 gram of undried substance was then treated by the combustion method; 0·0109 gram (=5·683 per cent.) of water was obtained, which, after subtracting 4·133 per cent. of water, leaves 0·172 per cent. of hydrogen. 0·096 per cent. of carbon was also found.

Several specimens of zirconium which had been melted in a vacuum electric furnace have been obtained and examined. The results vary somewhat among themselves; but this is due partly to difference in the substance before fusion, sometimes to an imperfect vacuum in the furnace, and also probably to variation in temperature and manipulation of the furnace.

The table shows some of the figures obtained:

	Zr obtained							
	as $ZrCl_4$.	as ZrO_2.	Total.	Oxygen.	Nitrogen.	Carbon.	Magnesium.	Total, per cent.
A......	83·85	11·70	95·55	4·14	absent	—	—	99·69
B......	73·70	17·49	91·19	6·17	2·02	0·084	0·28	99·744
			91·38*	6·17	2·02	0·084	0·28	99·934
C......	63·01	25·41	88·42	8·97	1·55	—	—	98·94
D......	24·79	53·68	78·47	18·95	much	—	—	97·42 + N

* By solution and precipitation.

A was bought from de Haen.

B was prepared by reduction of zirconium dioxide with magnesium at a high temperature, and afterwards melted in a vacuum electric furnace at the works of Messrs. E. de Haen, of Seelze.

C. Amorphous zirconium prepared by us under special precautions by the Berzelius process, and afterwards melted in a vacuum electric furnace by Messrs. Siemens and Halske, of Berlin. Much ash remained behind, and the fusion was repeated four or five times; in this way much of the oxide was removed.

D was prepared by the Berzelius process and subsequent fusion, at an earlier date than *C*.

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LVIII.—*The Preparation of Dichlorocarbamide.*

By Frederick Daniel Chattaway.

The author has recently shown (*Proc. Roy. Soc.*, 1908, *A*, **81**, 381) that when a solution of carbamide in water is acted on by chlorine, two of its hydrogen atoms are replaced by halogen, and dichlorocarbamide, $NHCl\cdot CO\cdot NHCl$, is formed.

If the chlorine is passed rapidly into a sufficiently concentrated solution, dichlorocarbamide crystallises out in thin, colourless plates, as it is much less soluble in water than the parent substance. The yield, however, is not good, even if the operation is carried out at a low temperature and as rapidly as practicable, the amount of dichlorocarbamide obtained thus never exceeds 25 per cent. of the quantity which should be furnished by the carbamide used, and is frequently much smaller, especially if the duration of the experiment has been unduly prolonged.

The loss is due mainly to hydrolysis of the dichlorocarbamide, which is much accelerated by the hydrogen chloride formed in the reaction:

$$NH_2\cdot CO\cdot NH_2 + 2Cl_2 = NHCl\cdot CO\cdot NHCl + 2HCl.$$

In this hydrolysis and the subsequent action of chlorine on the primary products, nitrogen chloride is formed, and can be recognised by its characteristic odour and the extraordinarily irritating quality of its vapour. As this nitrogen chloride is not only liberated during the passage of the chlorine, but is frequently found soaking the crystals of dichlorocarbamide when they are collected, the preparation of the latter may be a very disagreeable, although in no way a dangerous, operation.*

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* A very exaggerated idea of the danger of carrying out any operation in which nitrogen chloride is produced appears to be widely held, chiefly owing to Faraday's graphic description of a slight accident which befell him when experimenting with the substance before its properties were properly understood. In clean vessels and at the ordinary temperature considerable quantities of nitrogen chloride can be made either by the slow hydrolysis of dichlorocarbamide in aqueous solution, or by passing chlorine into an aqueous solution of an ammonium salt, without the slightest risk if ordinary precautions are taken. I have found it most convenient to prepare liquid nitrogen chloride by passing a slow stream of chlorine into a 20 per cent. solution of ammonium acetate through a tube reaching not quite to the bottom of the vessel. The nitrogen chloride then collects in a layer beneath the liquid, and can be washed by decantation and manipulated in quantities of 5 c.c. or thereabouts without risk. To render it perfectly safe, however, it may be diluted with two or three times its volume of chloroform, unless the presence of the latter is inadmissible.

Nitrogen chloride is very volatile in a current of air, and if the vapour only is needed, this can rapidly be drawn off and led through any desired solution by

If the hydrogen chloride set free in the reaction be removed as it is formed, so that the liquid is never strongly acid, this hydrolysis is to a large extent prevented, and a yield of dichlorocarbamide approaching the theoretical can be obtained, the loss under such conditions being chiefly due to the solubility of the compound in water.

The substance which has been found most effective for this purpose is zinc oxide. By the following procedure more than 75 per cent. of the theoretical yield of pure, dry, well-crystallised dichlorocarbamide can be obtained.

Six grams of carbamide are dissolved in 50 c.c. of distilled water, and 10 grams of finely divided zinc oxide are added. The mixture is cooled to -5° or thereabouts in a freezing mixture, and a rapid stream of chlorine passed through the liquid. If the operation is carried out in a small flask, and this is well shaken in the freezing mixture during the passage of the gas, the temperature does not rise above zero. The zinc oxide quickly dissolves, and a clear liquid results, from which in a very short time crystals of dichlorocarbamide begin to separate. When the liquid has become a thick pulp from the separated solid, and crystals appear no longer to separate, the dichlorocarbamide is rapidly collected by the aid of a pump, washed twice with 5 c.c. of ice-cold distilled water, and then several times with dry chloroform. The latter, in which dichlorocarbamide is only very slightly soluble, removes most of the adhering moisture. Ten grams of dichlorocarbamide are invariably obtained thus as a soft, white, crystalline powder. This yield is 77·5 per cent. of the theoretical.

The crystalline dichlorocarbamide thus obtained is pure, save for a scarcely recognisable amount of zinc chloride retained by the traces of mother liquor. For many purposes, the solid, simply filtered off or dried thus with chloroform, may be employed. The last traces of moisture can be removed by exposure in a vacuum for a short time over phosphoric oxide. A specimen thus obtained and dried gave the following numbers on analysis:

0·3389 liberated $I = 104{\cdot}2$ c.c. $N/10$-iodine. Cl as $\colon NCl = 54{\cdot}49$.

$CH_2ON_2Cl_2$ requires Cl as $\colon NCl = 54{\cdot}96$ per cent.

In order to ascertain how far the loss still observed is due to hydrolysis and how far to the dichlorocarbamide formed remaining dissolved in the mother liquor, an estimation of the solubility of the compound in water at 0° was made. An excess of dichloro-

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bubbling a stream of air through the water or ammonium acetate solution containing the liquid nitrogen chloride in suspension. In working with nitrogen chloride the effects of its vapour on the eyes and lungs, which are very painful and do not pass off for days, are far more to be feared than an explosion.

carbamide was shaken for an hour with distilled water in a thermostat at 0°. A known weight of solution was then filtered off, and the amount of dissolved dichlorocarbamide was estimated by adding excess of hydriodic acid and titrating the iodine liberated by standard thiosulphate. It was found that 100 grams of water at 0° dissolve 4 grams of dichlorocarbamide.

This determination of the solubility cannot lay claim to very great accuracy; indeed, this is impossible, since hydrolysis slowly goes on during the time taken by the operation, and at the end of the hour's shaking nitrogen chloride can be recognised by its odour, but still it is sufficiently exact for the purpose. Since from six grams of carbamide 10 grams of dichlorocarbamide can be obtained by the procedure above described, the difference between this amount and the theoretical yield of 12·9 grams, that is, 2·9 grams, has to be accounted for. Of this, 2·4 grams are held in solution in the mother liquor, assuming that the solubility of dichlorocarbamide in a dilute solution of zinc chloride does not differ markedly from its solubility in water; only about half a gram, therefore, undergoes hydrolysis during the process.

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LIX.—*The Alkaloids of Senecio latifolius.*

By HENRY EDGAR WATT, D.Sc. (Dunelm.).

ON account of the alleged poisonous effects on cattle, a number of plants from Cape Colony are being investigated in the Scientific and Technical Department of the Imperial Institute at the request of the Government of Cape Colony. Among these is *Senecio latifolius* (N.O. *Compositae*), a plant of common occurrence in certain parts of Cape Colony and the Transvaal. It is described by Cheeseman (*Manual of New Zealand Flora*, 1906, 374) as "a tall, erect, much-branched glabrous herb, two to four feet high; stem, flexuous, grooved. Leaves, membraneous, two to eight inches long, very variable in shape."

Several members of the Senecio, or "Ragwort," genus have, from time to time, been proved to have caused the death of cattle, thus suggesting the presence of a toxic constituent. In the *Annual Report of the New Zealand Department of Agriculture* (1902, 300) an account is given of the occurrence of "Winton disease" in horses and cattle, and this disease, in reality acute cirrhosis of the liver, is shown to be due to the consumption of *Senecio jacoboeus.* In the *Cape Agricultural Journal* (1904, 675), the administration of *Senecio Burchellii* to cattle is shown to have brought about all the symptoms of "Winton disease," and ultimately to have caused death. Finally, the Director of Agriculture for Cape Colony (*Report*, 1906, 41), referring to an outbreak of the same disease, says, "I have no doubt the cause is due to some plant or plants which are eaten, and which produce the action slowly," and adds that *Senecio latifolius*, a plant which has been experimentally proved to kill horses, grows profusely throughout the area.

In chemical literature, the only record of a chemical examination of members of the Senecio genus is contained in a paper by Grandval and Lajoux (*Compt. rend.*, 1895, **120**, 1120). These authors state that they have made an examination of *Senecio vulgaris* (the common groundsel) and have obtained from it two new alkaloids, to which they give the names *senecionine* and *senecine.* The former, to which they assign the formula $C_{18}H_{26}O_6N$, is stated to crystallise in rhombic plates, and to have a rotatory power of $[\alpha]_D - 80°49'$. No other data regarding it are given, and no crystalline salts were prepared. The second alkaloid, which was not obtained in a crystalline state and to which a formula is not given, is stated to form an acid tartrate and to be more soluble in ether and more bitter than senecionine.

The materials used in the present investigation consisted of two small supplies of *Senecio latifolius* received from the Agricultural Department of Cape Colony, one being collected before flowering, and the other after flowering.

EXPERIMENTAL.

Preliminary Examination.—Small portions of each sample of the coarsely-powdered plant were submitted to a systematic preliminary examination with a view to ascertain whether, or not, any substances of a glucosidic, phenolic, or resinous character, and likely to be physiologically active, were present; this work gave negative results, and attention was therefore directed to a search for alkaloids. The method adopted was that usually employed for the extraction of alkaloids, namely, the substance was exhausted with alcohol, the alcoholic extract distilled to remove alcohol, and the residue extracted with dilute acid; the acid solution was rendered alkaline with ammonia and extracted with chloroform, and finally the chloroform solution was distilled to dryness. When treated in this manner, both samples of the plant yielded dark-coloured, varnish-like residues, which were basic in character, and gave the usual alkaloidal reactions;

thus, with Mayer's reagent, a solution of the residue in dilute hydrochloric acid gave a white, flocculent precipitate, soluble in excess of the reagent; with Wagner's reagent, a similar acid solution gave a brown, crystalline periodide; and with gold chloride, a canary-yellow precipitate was obtained. In the case of *Senecio latifolius* "before flowering," the yield of crude alkaloidal residue amounted to 1·72 per cent., whilst in that of the "after flowering" sample it amounted to 0·76 per cent. These residues were subsequently dissolved in dilute acid, the solution so obtained rendered alkaline with ammonia and extracted with ether; on removal of the ether by distillation, they were obtained almost colourless, but still amorphous, and the weights of the purer materials represented percentages of 1·20 and 0·49 respectively on the two samples.

Isolation of an Alkaloid.

The whole quantity of each of the two samples of the plant was now coarsely powdered and separately exhausted with cold alcohol (95 per cent.) by percolation. As it was ultimately found that both samples contained the same alkaloids, a description of the methods adopted for the treatment of one of them will suffice.

The alcohol was removed from the alcoholic extract by distillation under diminished pressure, and the residue, when cold, treated with two per cent. hydrochloric acid. The acid solution was filtered and thoroughly shaken with ether, in order to remove colouring matter, etc.; it was then rendered alkaline with ammonia, and the alkaline liquor extracted with successive quantities of chloroform. The solution in chloroform was now extracted with 2 per cent. hydrochloric acid, and the acid solution so obtained was rendered alkaline with ammonia and shaken with chloroform. This solution in chloroform was washed with a small quantity of water, in order to remove traces of alkali, and, after removal of the solvent by distillation, the alkaloidal substance was obtained as a yellowish-brown, varnish-like mass.

The crude alkaloidal residue was neutralised exactly with one per cent. nitric acid; this solution was filtered and allowed to evaporate in a vacuous desiccator, by which means fine white crystals, together with a certain amount of non-crystalline matter, were obtained. The whole was dissolved in hot absolute alcohol, and, on cooling, crystals of a nitrate separated; after four crystallisations from absolute alcohol, the nitrate was obtained in colourless, elongated, rhombic prisms melting and decomposing at 240°.

The nitrate was dissolved in water, the solution rendered alkaline with ammonia, and extracted with ether. The ethereal solution was washed with a little water to remove traces of alkali, and dried over anhydrous sodium sulphate; the solvent was then removed by distillation, and a colourless, varnish-like residue remained. On dissolving this residue in chloroform and cautiously adding light petroleum, the free base separated in colourless, rhombic plates. It is proposed to name this alkaloid *senecifoline.*

Properties of Senecifoline.

Senecifoline is soluble in chloroform, ether, or alcohol, but is practically insoluble in light petroleum or water; it possesses a slightly bitter taste. With sulphuric acid, sulphuric acid and manganese dioxide, or with nitric acid, it gives no coloration. When, however, a drop of ferric chloride solution, and subsequently a drop of potassium ferricyanide solution, are added to an aqueous solution of the nitrate of the base, a greenish-blue coloration is obtained. Senecifoline darkens slightly when heated to 190°, and melts at 194—195°.

A solution of the alkaloid in alcohol is dextrorotatory. Determinations of the specific rotation were made in a Laurent's half-shadow polarimeter, and gave the following result as the mean of six readings:

$$a^{(22^\circ)} = +\ 1^\circ 5',\ c = 3{\cdot}85,\ l = 1\text{-dcm.};\ \text{whence}\ [a]_D + 28^\circ 8'.$$

When heated at 105°, 0·1718 lost 0·0008; the alkaloid therefore crystallises uncombined with its solvent. Analysis of the free base gave the following results:

0·1060 gave 0·2187 CO_2 and 0·0667 H_2O. C = 56·2; H = 7·0.
0·1258 ,, 4·36 c.c. N_2 (moist) at 20° and 766 mm. N = 4·0.
$C_{18}H_{27}O_8N$ requires C = 56·1; H = 7·0; N = 3·7 per cent.

Perkin's modification of Zeisel's method for the determination of methoxyl groups (Trans., 1903, **83**, 1367) was applied to the alkaloid, but no indication of the presence of such groups could be obtained; on cooling, however, a crystalline substance was seen to have separated from the hydriodic acid. This was collected and recrystallised from absolute alcohol, when white crystals melting at 210° were obtained. The amount of substance so obtained was too small to allow of further investigation, but, as will be evident later, it did not consist of the hydriodide of the base.

If an aqueous solution of the nitrate of the base is rendered alkaline with sodium hydroxide, the free base can be obtained by extraction with ether and subsequent removal of the ether by distillation; hence it follows that the alkaloid does not contain any phenolic hydroxyl groups.

Salts of Senecifoline.

Senecifoline nitrate is prepared by neutralising the crude alkaloidal residue with one per cent. nitric acid as previously described; the solution is allowed to evaporate spontaneously in a vacuous desiccator, and the pure nitrate is obtained from the residue by recrystallisation from absolute alcohol until the melting point is constant. It crystallises in colourless, elongated, rhombic prisms, and melts and decomposes at 240°. It is fairly soluble in cold, and very soluble in hot, water; it dissolves in hot absolute alcohol, but is very sparingly soluble in the cold solvent; it is insoluble in ether, chloroform, or light petroleum.

A solution of the salt in water is lævorotatory. The following result is the mean of six readings:

$$a^{(20^\circ)} = 0^\circ 30', \ c = 3{\cdot}165, \ l = 1\text{-dcm.}; \text{ whence } [a]_D - 15^\circ 48'.$$

When heated at 100—105°, 0·3190 lost 0·0020; the salt therefore crystallises uncombined with its solvent.

Senecifoline hydrochloride was prepared by dissolving the pure base in sufficient dilute hydrochloric acid to produce a neutral solution, and allowing this to evaporate in a vacuous desiccator, when a white, crystalline residue was obtained. This was dissolved in hot absolute alcohol, and caused to crystallise by the addition of sufficient ether to make the solution slightly cloudy; after some time, crystals of the hydrochloride separated in fine white needles, which melted and decomposed at 260°. Senecifoline hydrochloride is much more soluble in water or alcohol than the nitrate; it resembles the latter, however, in that it is quite insoluble in ether, chloroform, or light petroleum. A solution of the salt in water is lævorotatory; the following result is calculated from the mean of six readings:

$$a^{(20^\circ)} = -0^\circ 13', \ c = 1{\cdot}08, \ l = 1\text{-dcm.}; \text{ whence } [a]_D - 20^\circ.$$

When heated at 100—105°, 0·0748 lost 0·0003; the salt therefore crystallises uncombined with its solvent.

Senecifoline hydriodide was obtained as a white, crystalline precipitate by the interaction of the nitrate and potassium iodide in aqueous solution; it was collected, washed with a little water, dried, and recrystallised from absolute alcohol. The hydriodide thus prepared crystallised in flat plates—probably monoclinic—and melted and decomposed at 248°; it is much less soluble in water or alcohol than the nitrate.

Senecifoline aurichloride.—By the addition of an aqueous solution of gold chloride to an aqueous solution of senecifoline hydrochloride acidified with hydrochloric acid, a bright canary-yellow, amorphous precipitate was obtained. The salt was collected, washed with water until free from acid, and dried in a vacuous desiccator. It was readily obtained in golden, lath-shaped crystals—probably belonging to the rhombic system—by recrystallisation from absolute alcohol. As thus prepared, it crystallises with one molecule of alcohol, as shown by the following determination:

0·2455 lost, at 105°, 0·0142. $C_2H_6O = 5{\cdot}78$.

$C_{18}H_{27}O_8N,HAuCl_4,C_2H_6O$ requires $C_2H_6O = 5{\cdot}96$ per cent.

The salt, dried at 105°, melts and decomposes at 220°.

A known weight of the aurichloride, dried at 105°, was suspended in water, and hydrogen sulphide passed through the liquid until the whole of the salt was decomposed. The sulphide was collected, dried, ignited, and the gold weighed as metal:

0·2940 gave 0·0787 Au. $Au = 26{\cdot}77$.

Another portion of the salt, dried at 105°, was directly ignited and gave the following result:

0·1160 gave 0·0313 Au. $Au = 27{\cdot}16$.

$C_{18}H_{27}O_8N,HAuCl_4$ requires $Au = 27{\cdot}17$ per cent.

Decomposition of Senecifoline by Alkali.

An experiment was made to ascertain whether, or not, senecifoline could be hydrolysed in two stages in the same manner as indaconitine (Dunstan and Andrews, Trans., 1905, **87**, 1620). The pure base (0·3850 gram) was dissolved in the requisite amount of *N*/10-sulphuric acid to form the neutral sulphate, and the solution was heated in a sealed tube to 125—130° for six hours. After cooling, the contents of the tube gave a neutral reaction; the solution was rendered alkaline with ammonia, and extracted with ether; the ethereal solution was then distilled, when practically the whole of the pure base was recovered. This was converted into the nitrate, which, by determination of the melting point and specific rotation, was found to be identical with senecifoline nitrate. No hydrolysis had therefore been effected.

Another portion of the pure base (2 grams) was dissolved in 50 c.c. of absolute alcohol, and 4 c.c. of a 40 per cent. solution of sodium hydroxide were added. After twenty-four hours, the liquid was neutralised with hydrochloric acid, and the alcohol removed by distillation under diminished pressure; the residue was dissolved in a small quantity of water, the solution acidified with hydrochloric acid and extracted with ether, and the ethereal solution washed with a little water, dried, and concentrated to a small bulk by distillation. On standing, colourless crystals gradually separated from the solution. The substance so obtained was shown to exhibit acidic properties, and the name *senecifolic acid* is suggested for it.

Properties of Senecifolic Acid.

Senecifolic acid is soluble in chloroform, ether, or alcohol, sparingly so in water, and insoluble in light petroleum. It possesses a slightly acid taste, crystallises in colourless, six-sided plates belonging to the rhombic system, and melts at 198—199°. A solution of the acid in alcohol is dextrorotatory. The following result is the mean of six readings:

$a^{(20°)} = +0°25'$, $c = 1·468$, $l = 1$-dcm.; whence $[a]_D + 28°22'$.

When heated at 105°, 0·1488 lost 0·0020; the acid therefore crystallises uncombined with its solvent.

Senecifolic acid does not contain nitrogen. On analysis:

0·1922 gave 0·3642 CO_2 and 0·1220 H_2O. C = 51·68; H = 7·05.

$C_{10}H_{16}O_6$ requires C = 51·72; H = 6·9 per cent.

By the addition of an aqueous solution of silver nitrate to an aqueous solution of the sodium salt of senecifolic acid, prepared by neutralising the acid with sodium hydroxide, a white, flocculent precipitate of the *silver* salt was obtained. This was sparingly soluble in hot water, and crystallised in needles on cooling. The salt was collected, washed with water, and dried in a vacuous desiccator. On ignition:

0·1514 gave 0·0724 Ag. Ag = 47·82.

$C_{10}H_{14}O_6Ag_2$ requires Ag = 48·43 per cent.

By titration of the free acid with *N*/10-sodium hydroxide, using phenolphthalein as indicator, the following result was obtained:

0·1203 required 9·25 c.c. Na = 17·6.

$C_{10}H_{16}O_6$ requires Na = 20·0 per cent.

The end reaction was exceedingly indefinite.

The molecular weight of senecifolic acid was determined by the cryoscopic method:

0·1455 in 11·0807 glacial acetic acid gave $\Delta t = -0·190°$. M.W. = 263.

$C_{10}H_{16}O_6$ requires M.W. = 232.

When a drop of a one per cent. solution of potassium permanganate is added to a neutral solution of the sodium salt of the acid, no immediate decoloration takes place; hence senecifolic acid does not appear to contain an ethylenic linking, and, in view of this fact, it is probably a monocyclic dihydroxydicarboxylic acid. Moreover, since no dibasic acid of the formula $C_{10}H_{16}O_6$, and possessing the properties referred to above, has been previously described, senecifolic acid must be regarded as a new substance.

The acid solution which remained after the extraction of senecifolic acid and contained the remaining product of hydrolysis, was rendered alkaline by sodium hydroxide and extracted with chloroform; the chloroform was then evaporated, but no residue was obtained. Thus it was proved that hydrolysis of the original base was complete, and that the hydrolytic base was too soluble in water to be extracted by chloroform; in this respect it resembles other bases obtained by the hydrolysis of alkaloids of the ester type, such as ecgonine from cocaine and aconine from aconitine.

The alkaline liquid was then neutralised with hydrochloric acid, and evaporated to dryness under diminished pressure; the dry residue, which contained a considerable amount of sodium chloride, was extracted with three or four successive portions of absolute alcohol, and the solution was evaporated in a vacuous desiccator. By this means, crystals of a *hydrochloride* were obtained, and it is proposed to name the corresponding base *senecifolinine.*

Properties of Senecifolinine Hydrochloride.

Senecifolinine hydrochloride is readily soluble in water or alcohol, but insoluble in chloroform, ether, or light petroleum. On recrystallisation from absolute alcohol it is obtained in colourless, rhombic prisms melting at 168°.

A solution of the salt in water is lævorotatory:

$$\alpha^{(20^\circ)} = -0^\circ 11', c = 1{\cdot}455, l = 1\text{-dcm.}; \text{ whence } [\alpha]_D -12^\circ 36'.$$

When heated at 105°, 0·1536 lost 0·0020; the salt therefore crystallises uncombined with its solvent.

On analysis, the following result was obtained:

0·1565 gave 0·2864 CO_2 and 0·1022 H_2O. C = 49·9; H = 7·2.

$C_8H_{11}O_2N,HCl$ requires C = 50·66; H = 6·33 per cent.

The figure for hydrogen is somewhat high, but this may be explained by the fact that the salt is hygroscopic.

By titration of a solution of senecifolinine hydrochloride with *N*/10-silver nitrate, the following result was obtained:

0·0378 required 2·0 c.c. $C_8H_{11}O_2N,HCl$ requires 2·0 c.c.

Other Salts of Senecifolinine.

Senecifolinine nitrate was prepared by adding the theoretical quantity of an aqueous solution of silver nitrate to an aqueous solution of senecifolinine hydrochloride. After removing silver chloride, the solution was evaporated to dryness in a vacuous desiccator. The nitrate thus obtained was extremely hygroscopic, and could not be obtained in a definite crystalline form.

Senecifolinine aurichloride.—By the addition of an aqueous solution of gold chloride to an aqueous solution of senecifolinine hydrochloride acidified with hydrochloric acid, a bright canary-yellow, crystalline precipitate was obtained. The salt was collected, washed with water until free from acid, and dried in a vacuous desiccator. The aurichloride was obtained in elongated, rhombic prisms by cautiously adding light petroleum to its solution in absolute alcohol. Senecifolinine aurichloride is much more soluble in water or alcohol than the corresponding salt of senecifoline, and is insoluble in light petroleum. It melts at 150°.

When heated at 105°, 0·1370 lost 0·0005; the salt therefore crystallises uncombined with its solvent.

The amount of gold in the salt was estimated by passing hydrogen sulphide through its aqueous solution:

0·1403 gave 0·0560 Au. Au = 39·9.

$C_8H_{11}O_2N,HAuCl_4$ requires Au = 39·96 per cent.

Isolation of a Second Alkaloid.

The alcoholic mother liquor, from which senecifoline nitrate was crystallised, was concentrated to a small bulk, and decanted from the crystalline nitrate which had separated; it was then evaporated in a vacuous desiccator, and obtained as a semi-solid, amorphous mass, which, after standing for several days, became crystalline. As the substance was now very dark in colour, it was dissolved in water, rendered slightly acid, and extracted with ether to remove colouring matter, etc.; the solution was then rendered alkaline with ammonia and extracted with chloroform. The chloroform solution was washed with a little water to remove traces of alkali, and, after removal of the solvent by distillation, the alkaloidal substance was obtained as a yellow, varnish-like mass. This was neutralised exactly with one per cent. nitric acid, the solution filtered, and allowed to evaporate in a vacuous desiccator, whereby the nitrate was again obtained as a semi-solid, amorphous mass, which, on long standing, became crystalline. The salt was then dissolved in the smallest possible quantity of absolute alcohol, and to this solution a small quantity of dry ether was cautiously added; the solution was set aside for three or four days, when a small amount of senecifoline nitrate was found to have separated; the supernatant liquid was decanted, and, on further keeping, colourless, needle-like crystals of a nitrate separated; these were purified by recrystallisation from a mixture of absolute alcohol and ether until the melting point was constant. The salt was dissolved in water, the solution rendered alkaline with ammonia, and extracted with ether. The ethereal solution was washed with a small quantity of water, dried, and the solvent removed by distillation, when a colourless, crystalline residue was obtained. This was purified by dissolving it in absolute alcohol and allowing the solution to evaporate spontaneously, when the free base was obtained in colourless, rhombic plates. The name *senecifolidine* is suggested for this alkaloid.

Properties of Senecifolidine.

Senecifolidine is less soluble in chloroform, ether, or alcohol than senecifoline, but resembles the latter in being insoluble in light petroleum or water; it possesses a slightly bitter taste. With sulphuric acid it gives a pink coloration, but no further colour is developed on the addition of manganese dioxide to the mixture. The nitrate of the base gives a greenish-blue coloration with a solution of ferric chloride and potassium ferricyanide solution, as described under senecifoline. When heated to 200° it darkens, and melts at 212°.

A solution of the alkaloid in alcohol is lævorotatory, as shown by the following result:

$$a^{(20°)} = -0°24',\ c = 2{\cdot}87,\ l = 1\text{-dcm.};\ \text{whence}\ [a]_D\ -13°56'.$$

When heated at 105° it did not lose in weight, and therefore crystallises uncombined with its solvent.

On analysis, the following results were obtained:

0·2017 gave 0·4368 CO_2 and 0·1266 H_2O. C = 59·06; H = 6·97.

0·1200 ,, 4·3 c.c. N_2 (moist) at 20° and 762 mm. N = 4·1.

$C_{18}H_{25}O_7N$ requires C = 58·9; H = 6·81; N = 3·81 per cent.

Salts of Senecifolidine.

Senecifolidine nitrate was obtained, as previously described, by fractional crystallisation from the mother liquor which remained after the crystallisation of senecifoline nitrate. It crystallises in colourless, acicular prisms belonging to the rhombic system, and melts at 145°. It is very readily soluble in water or absolute alcohol, but is insoluble in ether or chloroform.

An aqueous solution of the salt is lævorotatory, as shown by the following result:

$$a^{(20°)} = -0°37',\ c = 2{\cdot}532,\ l = 1\text{-dcm.};\ \text{whence}\ [a]_D\ -24°21'.$$

Senecifolidine nitrate crystallises with half a molecule of alcohol, as shown by the following determination:

0·2060 lost, at 105°, 0·0095. C_2H_6O = 4·6.

$(C_{18}H_{25}O_7N,HNO_3)_2,C_2H_6O$ requires C_2H_6O = 4·89 per cent.

Senecifolidine hydrochloride was prepared by dissolving the pure base in sufficient dilute hydrochloric acid to produce a neutral solution; this was allowed to evaporate in a vacuous desiccator, when a colourless, hygroscopic residue was obtained. Owing to the readiness with which it absorbed water, it was not isolated in a crystalline condition.

Senecifolidine aurichloride.—This salt was obtained as a bright canary-yellow, amorphous precipitate by the addition of an aqueous solution of gold chloride to an aqueous solution of senecifolidine hydrochloride acidified with hydrochloric acid. The salt was collected, washed with water until freed from acid, and dried in a vacuous desiccator; the pure salt was subsequently obtained in yellow, hair-like crystals by recrystallisation from absolute alcohol.

After heating at 105°, 0·1623 lost 0·0009; the salt therefore crystallises uncombined with its solvent.

The amount of gold in the salt was estimated by passing hydrogen sulphide through its aqueous solution, and treating in the same manner as in the case of the corresponding salt of senecifoline:

0·1614 gave 0·0448 Au. Au = 27·75.

$C_{18}H_{25}O_7N,HAuCl_4$ requires Au = 27·86 per cent.

Summary and Conclusions.

As a result of the present investigation, two new alkaloids have been added to the small number of such compounds which are known to occur in plants belonging to the N.O. Compositæ. The names *senecifoline* and *senecifolidine* are proposed for these alkaloids, and the formulæ $C_{18}H_{27}O_8N$ and $C_{18}H_{25}O_7N$ respectively assigned to them; thus it appears that the two substances differ by the elements of a molecule of water. Senecifoline has been hydrolysed by alkalis into a dibasic acid, $C_{10}H_{16}O_6$, for which the name *senecifolic acid* is suggested, and a base, $C_8H_{11}O_2N$, which it is proposed to term *senecifolinine*. The free base was not isolated.

From a consideration of the products of this action, it would appear that the reaction may be represented by the following equation:

$$C_{18}H_{27}O_8N + 2NaOH = C_{10}H_{14}O_6Na_2 + C_8H_{11}O_2N + 2H_2O,$$

which is analogous to the decomposition of atropine into atropic acid and tropine by means of barium hydroxide:

$$2C_{17}H_{23}O_3N + Ba(OH)_2 = (C_9H_7O_2)_2Ba + 2C_8H_{15}ON + 2H_2O.$$

The pharmacology of senecifoline and senecifolidine is being studied by Prof. A. R. Cushny, F.R.S., who has already found that the former is poisonous to animals.

It is hoped to proceed further in the investigation as soon as adequate supplies of material are available.

This investigation has been carried out in the laboratories of the

Scientific and Technical Department of the Imperial Institute, and I desire to express my indebtedness to Prof. Wyndham R. Dunstan, F.R.S., for the facilities which he has accorded me for carrying out the work.

Scientific and Technical Department,
Imperial Institute, S.W.

LX.—*Estimation of Primary, Secondary, and Tertiary Amines. Part I.*

By John Joseph Sudborough and Harold Hibbert.

In a short note published some years ago (Proc., 1904, **20**, 165) the authors outlined a general method for the quantitative estimation of amines, based on the measurement of the volume of methane evolved when these substances are caused to react with magnesium methyl iodide. It is only recently that a suitable opportunity has occurred for completing the work, and they are able to show that the method is capable of general application, not only for the estimation of primary and secondary amines, but also for the quantitative determination of mixtures of these with tertiary amines.

In a previous communication (Trans., 1904, **85**, 933) a similar method for estimating hydroxyl compounds was employed and satisfactory results were obtained in most cases. Zerewitinoff (*Ber.*, 1907, **40**, 2023) has shown that the process can be used for the most varied types of hydroxy-derivatives, and also for estimating the reactive hydrogen in other groups of compounds; for example, hydrosulphides, imides, amides (*Ber.*, 1908, **41**, 2233). In our earlier note (*loc. cit.*) it was stated that when a primary or secondary amine is brought in contact with excess of magnesium methyl iodide at the ordinary temperature, a reaction takes place in accordance with the following equations:

Primary amine: $R_1 \cdot NH_2 + CH_3 \cdot MgI = R_1NH \cdot MgI + CH_4$

Secondary amine: $R_1R_2NH + CH_3 \cdot MgI = R_1R_2N \cdot MgI + CH_4$,

that is, one molecule of the amine liberates one molecule of methane. If now the temperature is raised to 120—125°, no change occurs in the case of the secondary amine, but the magnesium derivative of the primary reacts with an excess of the Grignard reagent evolving a second molecule of methane.

With tertiary amines there is no evolution of gas either at the ordinary temperature or at 120°.

The majority of the experiments forming the present communication were carried out with phenetole as the solvent. This has the advantage over amyl ether in that it is much more easily purified, but as methane is soluble in it to an appreciable extent, it is necessary to perform a blank experiment with a known substance (for example, diphenylamine) in order to determine this constant.

As in the previous experiments, the air was displaced by nitrogen, although Zerewitinoff (*loc. cit.*) considers this unnecessary.

Preparation of the Magnesium Methyl Iodide Solution.

The phenetole was purified by shaking with alkali, then with water, and, after drying with calcium chloride, distilling over metallic sodium.

Dry magnesium turnings (6·09 grams) were added to 120 c.c. of the dry phenetole, and 35·5 grams of methyl iodide dissolved in 20 c.c. of the phenetole were then introduced. The mixture was heated gently on the sand-bath until the reaction commenced, and then the flame regulated so as to maintain a vigorous action. After about forty-five minutes, practically the whole of the magnesium had disappeared, and the contents were then heated to the boiling point for half an hour to expel any traces of uncombined methyl iodide. On cooling, the clear solution was decanted and made up to 175 c.c. with pure phenetole. The solution must be kept from contact with the atmosphere as much as possible.

The solution in amyl ether was prepared in the manner already described (*loc. cit.*, p. 934).

Estimation of Imino-groups.

The method adopted and the apparatus used are those already described for the estimation of hydroxyl groups (Trans., 1904, **85**, 933).

A stout flask of about 200 c.c. capacity is fitted with a doubly-bored indiarubber stopper, which carries a stopcock reaching nearly to the bottom of the flask, and a short tube which is fitted by means of a length of thick-walled indiarubber tubing to a Lunge nitrometer or Hempel burette filled with dry mercury.

Dry phenetole (5·0 c.c.) and 0·1—0·3 gram of the substance are placed in the flask, and an excess (7·5 c.c.) of the solution of magnesium methyl iodide in phenetole is placed in a small tube, which is lowered into the flask in a vertical position.

The air in the flask is displaced by dry nitrogen, the flask is then attached to a Hempel burette, filled with dry mercury, and the apparatus left for forty-five minutes to attain a constant temperature.

The height of the mercury, the temperature, and pressure are noted, and, after mixing the two solutions and shaking vigorously, the level of the mercury is adjusted and the volume read off with the usual precautions.

A blank experiment is necessary to determine the amount of methane absorbed by the phenetole. For this purpose we used phenyl-α-naphthylamine, and found that the volume absorbed under the given conditions amounted to 4·4 c.c.

The following imino-derivatives have been used: phenyl-α- and -β-naphthylamines, ββ-dinaphthylamine, diphenylamine, ethyl- and methyl-anilines.

No. of expt.	Substance.	Weight in mm.	Temp.	Pressure in mm.	Volume of gas in c.c.	Theory.
1.	Phenyl-α-naphthylamine	0·2638	12°	754	28·2	28·2
2.	Phenyl-β-naphthylamine	0·3136	13	756	35·5	33·6
3.	ββ-Dinaphthylamine	0·2810	14	746	26·9	24·9
4.	Diphenylamine	0·3100	14	746	42·8	43·7
5.	Ethylaniline	0·2132	14	756	41·9	41·4
6.	Methylaniline	0·1886	13	741	42·2	42·1

There was no further evolution of gas on warming to 120°.

Estimation of Amino-groups.

The same quantities of solvent and magnesium methyl iodide solution were taken as in the previous estimations, and the volume of gas evolved at the ordinary temperature was determined. The mixture was then heated in an oil-bath to 120—125° until no further evolution of gas took place, which occupied, in general, from forty-five to sixty minutes.

The air-pressure was kept approximately constant by adjusting the mercury column. After allowing to cool to the ordinary temperature, the volume of gas was read off as before.

No. of expt.	Substance.	Weight in gram.	Temp.	Pressure in mm.	Volume of gas in c.c.	Theory.
7.	β-Naphthylamine	0·2110	13·6	759	34·6	34·5
7*a*.	,,	0·2110	13·6	759	68·0	69·0
8.	*p*-Toluidine	0·1880	11·2	762·5	40·2	40·5
9.	,,	0·2084	13·2	767	43·7	45·0
9*a*.	,,	0·2084	13·2	767	87·7	90·0
10.	β-Chloroaniline	0·1812	16·0	743	33·8	34·3
11.	,,	0·1472	16·0	744	27·8	27·8
11*a*.	,,	0·1472	16·0	744	54·4	55·6

(In experiments 7*a*, 9*a*, and 11*a* the mixture was heated to 120—125° until no further evolution of gas took place.)

Tertiary Amines.

With the following tertiary amines there was no gas evolved under the above conditions, either at the ordinary temperature or at 125°, namely, dimethylaniline, diethylaniline, and tetramethyl-*p*-diaminodiphenylmethane.

Notes on the Experiments.

Estimations 7, 8, and 9 were performed in amyl-ethereal solution, but in all the other experiments phenetole was used as solvent. The substances investigated, as well as the reaction products, are readily soluble in phenetole. It was noticeable that the amino- and iminobenzene derivatives react most readily, the benzene-naphthalene derivatives less so, and the dinaphthylamine least readily, so that it was necessary with the latter substances to shake for some time before all the methane was evolved.

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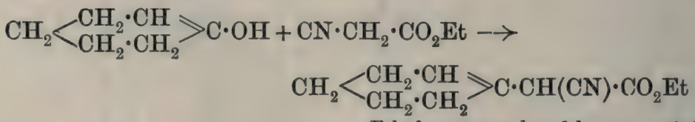
LXI.—*The Condensation of Ketones and Aldehydes with the Sodium Derivative of Ethyl Cyanoacetate.*

By WALTER NORMAN HAWORTH.

IN a previous communication (Trans., 1908, 93, 1944) Harding, Haworth, and Perkin published an account of the condensation of ethyl cyanoacetate with *cyclo*hexanone and certain of its homologues, and it was shown that *cyclo*hexanone condenses in its enolic form with ethyl cyanoacetate, thus:

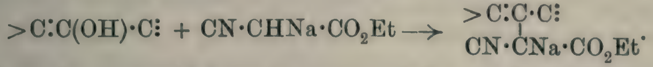


$$CH_2\left<\begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH_2\end{matrix}\right>C\cdot OH + CN\cdot CH_2\cdot CO_2Et \longrightarrow CH_2\left<\begin{matrix}CH_2\cdot CH\\ CH_2\cdot CH_2\end{matrix}\right>C\cdot CH(CN)\cdot CO_2Et$$

Ethyl α-cyano-Δ^1-*cyclo*hexene-acetate.

This interesting reaction has been extended and found to be quite general in its application to such ketones and aldehydes, both in the aliphatic and aromatic series, which are capable of tautomeric change into the enolic form. In the case of ketones such as benzophenone, $C_6H_5\cdot CO\cdot C_6H_5$, which is incapable of providing the necessary hydrogen atom for tautomeric change, the reaction does not proceed.

As has already been pointed out (*loc. cit.*), the general course of the reaction may be expressed in the following manner:



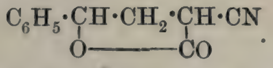
$$>C{:}C(OH){\cdot}C\vdots + CN{\cdot}CHNa{\cdot}CO_2Et \longrightarrow \begin{array}{l} >C{:}C{\cdot}C\vdots \\ \quad | \\ CN{\cdot}CNa{\cdot}CO_2Et \end{array}$$

When phenylacetaldehyde is employed, the condensation proceeds quite normally, with the formation of *ethyl α-cyano-α-styrylacetate*,

$$C_6H_5{\cdot}CH{:}CH{\cdot}OH + HCNa(CN){\cdot}CO_2Et \longrightarrow C_6H_5{\cdot}CH{:}CH{\cdot}CNa(CN){\cdot}CO_2Et.$$

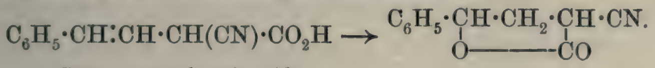
On acidifying, the *sodium* derivative is decomposed, and the ester distils at 195—197°/20 mm. as a viscid, yellow oil. That the ester contains a double linking in the place assigned to it in the above formula is shown by the fact that the molecule possesses a reactive hydrogen atom replaceable by sodium. By condensing the sodium compound with ω-bromoacetophenone, a solid substitution product is obtained, namely, *ethyl α-cyano-β-benzoyl-α-styrylpropionate*, which melts at 110° (p. 484).

Ethyl α-cyano-α-styrylacetate yields on hydrolysis with potassium hydroxide in methyl-alcoholic solution the *lactone* of *α-cyano-γ-hydroxy-γ-phenylbutyric acid*,



$$\begin{array}{l} C_6H_5{\cdot}CH{\cdot}CH_2{\cdot}CH{\cdot}CN \\ \qquad O\text{———}CO \end{array}.$$

The formation of this substance, which melts at 90°, is probably due to the addition of water at the double linking and the subsequent elimination of water according to the scheme:



$$C_6H_5{\cdot}CH{:}CH{\cdot}CH(CN){\cdot}CO_2H \longrightarrow \begin{array}{l} C_6H_5{\cdot}CH{\cdot}CH_2{\cdot}CH{\cdot}CN. \\ \qquad O\text{———}CO \end{array}$$

α-Cyano-α-styrylacetic acid.

Another substance was also isolated in small amount from the product of the condensation of ethyl cyanoacetate with phenylacetaldehyde, namely, *αα′-dicyano-β-benzylglutaric acid*,

$$CO_2H{\cdot}CH(CN){\cdot}CH(CH_2{\cdot}C_6H_5){\cdot}CH(CN){\cdot}CO_2H,$$

a colourless, crystalline substance, which melts at 173°.

Another condensation which was investigated was that of benzylideneacetone with ethyl cyanoacetate, and in this case the reaction proceeded normally with the formation of *α-cyano-β-styryl-β-methylacrylic acid*,

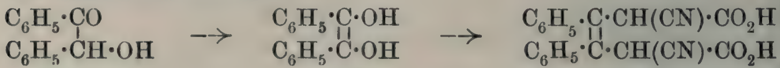
$$C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}CH{:}CH{\cdot}CMe{:}C(CN){\cdot}CO_2H.$$

This unsaturated cyano-acid melts at 188° with evolution of carbon dioxide. On treatment with potassium hydroxide, it yields the corresponding *carboxyamide*, m. p. 166°, and this may then be further hydrolysed to *β-styryl-β-methylacrylic acid*,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CO_2H,$$

which melts at 190°.

It was next thought that it would be interesting to investigate the condensation of ethyl cyanoacetate with a ketone containing an adjacent secondary alcohol group, and benzoin was selected. It was found that the condensation gave rise to a remarkable product containing two cyano-acid residues, the course of the reaction evidently taking place according to the scheme:



$$\begin{array}{l} C_6H_5\cdot CO \\ \quad\;\; | \\ C_6H_5\cdot CH\cdot OH \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot C\cdot OH \\ \quad\;\; \Vert \\ C_6H_5\cdot C\cdot OH \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot C\cdot CH(CN)\cdot CO_2H \\ \quad\;\; \Vert \\ C_6H_5\cdot C\cdot CH(CN)\cdot CO_2H \end{array}$$

Benzoin. Enolic form. *αδ-Dicyano-βγ-diphenyl-Δ^{β}-butene-αδ-dicarboxylic acid.*

This dicyano-acid is a colourless, crystalline substance, which melts and decomposes at 136°, and yields sparingly soluble *sodium* and *potassium* derivatives.

Acetophenone condenses readily with ethyl cyanoacetate, but the reaction does not proceed in a simple manner, and the following is probably the correct explanation of the course which the condensation takes:

$$CH_2{:}C(C_6H_5)\cdot OH + HCNa(CN)\cdot CO_2Et \longrightarrow$$

Acetophenone (enolic form).

$$CH_2{:}C(C_6H_5)\cdot CNa(CN)\cdot CO_2Et.$$

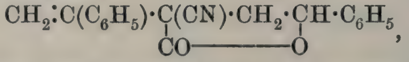
This sodiocyano-ester then reacts with a second molecule of acetophenone, the following additive process taking place:

$$CH_2{:}C(C_6H_5)\cdot CNa(CN)\cdot CO_2Et + CH_2{:}C(OH)\cdot C_6H_5 \longrightarrow$$

$$CH_2{:}C(C_6H_5)\cdot C(CN)(CO_2H)\cdot CH_2\cdot CH(OH)\cdot C_6H_5.$$

γ-Cyano-ε-hydroxy-βε-diphenyl-Δ^{α}-pentene-γ-carboxylic acid.

The hydroxy-acid thus obtained is unstable, and passes with extreme readiness into the *lactone*,



$$\begin{array}{l} CH_2{:}C(C_6H_5)\cdot C(CN)\cdot CH_2\cdot CH\cdot C_6H_5 \\ \qquad\qquad\qquad\;\; | \qquad\qquad\quad | \\ \qquad\qquad\qquad CO\text{———————}O \end{array},$$

which is crystalline, and melts at 157°. This lactone is the principal product of the condensation, but *γ-cyano-ε-hydroxy-βε-diphenyl-Δ^{β}-pentene*, $C_6H_5\cdot CMe{:}C(CN)\cdot CH_2\cdot CH(OH)\cdot C_6H_5$, b. p. 225°/13 mm., and *γ-cyano-βε-diphenyl-$\Delta^{\beta\delta}$-pentadiene*, $C_6H_5\cdot CMe{:}C(CN)\cdot CH{:}CH\cdot C_6H_5$, b. p. 210°/13 mm., are also formed in considerable quantities.

EXPERIMENTAL.

Ethyl α-Cyano-α-styrylacetate, $C_6H_5\cdot CH{:}CH\cdot CH(CN)\cdot CO_2Et$, *and its Derivatives.*

In order to prepare this substance, ethyl cyanoacetate (11·5 grams) is mixed with a solution of sodium (2·3 grams) in ethyl alcohol (28 grams), when the solid sodium derivative of ethyl cyanoacetate separates from the solution.

Without cooling the mixture, phenylacetaldehyde (12 grams) is added; almost immediately the white sodium compound disappears, forming a clear yellow solution, and, by heating on the water-bath, a yellow sodium derivative gradually separates. After heating for an hour, the product is allowed to cool, and sufficient water is added to dissolve completely the contents of the flask. The solution is now acidified with dilute hydrochloric acid, and the oil, which is precipitated, is extracted with ether, the ethereal extract is washed twice with water to free it from alcohol, and then shaken with aqueous sodium carbonate solution (*A*) in order to separate the acid which is always formed during the condensation. After this treatment the ethereal solution is dried and evaporated, and the residual oil fractionated under diminished pressure. A little unchanged phenylacetaldehyde is always present, and after this has passed over, the *ethyl a-cyano-a-styrylacetate* distils constantly at 195—197°/20 mm. as a viscid, yellow oil:

0·1660 gave 0·4390 CO_2 and 0·0970 H_2O. C = 72·2; H = 6·4.
0·1553 „ 8·5 c.c. N_2 at 12° and 768 mm. N = 6·6.
$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·0; N = 6·5 per cent.

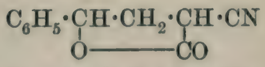
Hydrolysis.—The hydrolysis of the above ester is effected by digesting it for a few minutes with twice the theoretical amount of potassium hydroxide dissolved in methyl alcohol. On adding water and acidifying, a semi-solid mass is precipitated, which, when placed on a porous tile, soon becomes quite hard and can then be recrystallised from dilute methyl alcohol, from which the substance separates in minute prisms melting at about 90°.

It was at once evident that this substance is not an acid, for although obtained from an alkaline solution by acidifying, it will not again dissolve in cold alkalis. On boiling with aqueous sodium carbonate, it gradually dissolves, and is reprecipitated on acidifying. This behaviour indicates that the substance is a lactone, and its formation is probably due to the addition of water at the double linking and subsequent elimination of water according to the scheme:

$$C_6H_5\cdot CH{:}CH\cdot CH(CN)\cdot CO_2H \longrightarrow$$

α-Cyano-α-styrylacetic acid.

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH(CN)\cdot CO_2H \longrightarrow$$



$$C_6H_5\cdot\underset{\underset{O}{|}}{CH}\cdot CH_2\cdot\underset{\underset{CO}{|}}{CH}\cdot CN$$

α-Cyano-γ-hydroxy-γ-phenylbutyric acid.

Lactone of α-cyano-γ-hydroxy-γ-phenylbutyric acid.

0·0807 gave 0·2090 CO_2 and 0·0370 H_2O. C = 70·6; H = 5·1.
0·1100 ,, 6·8 c.c. N_2 at 15° and 762 mm. N = 7·3.
$C_{11}H_9O_2N$ requires C = 70·6; H = 4·8; N = 7·5 per cent.

The *lactone* of *α-cyano-γ-hydroxy-γ-phenylbutyric acid* melts at about 90°, and is readily soluble in methyl or ethyl alcohol or benzene, but sparingly so in light petroleum. It dissolves in concentrated sulphuric acid, yielding an intense red coloration; the same phenomenon is observed when the corresponding ester, ethyl α-cyano-α-styrylacetate, is similarly treated. As this seems to be due to some internal condensation of the molecule, it is at present being further investigated.

Ethyl α-Cyano-β-benzoyl-α-styrylpropionate, $C_6H_5\cdot CH\colon CH\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CO\cdot C_6H_5$.

This substance was prepared with the object of demonstrating the presence of a reactive hydrogen atom replaceable by various substituting groups in the molecule of ethyl α-cyano-α-styrylacetate. The ester was converted into its sodium derivative by mixing with an equivalent amount of sodium ethoxide in ethyl-alcoholic solution, and an equivalent proportion of ω-bromoacetophenone dissolved in ethyl alcohol was then added. Sodium bromide soon separated, and, after warming for a few minutes, water was added until the solution became slightly cloudy, when, after several hours, the product separated in a crystalline condition. It crystallises from methyl alcohol in minute, colourless plates, which melt at 110° and dissolve in concentrated sulphuric acid with a red coloration:

0·1276 gave 0·3540 CO_2 and 0·0720 H_2O. C = 75·7; H = 6·2.
$C_{21}H_{19}O_3N$ requires C = 75·7; H = 5·7 per cent.

αα′-Dicyano-β-benzylglutaric Acid, $CO_2H\cdot CH(CN)\cdot CH(CH_2\cdot C_6H_5)\cdot CH(CN)\cdot CO_2H$.

This dibasic acid is isolated from the sodium carbonate extract *A* (p. 483) by acidifying with mineral acid and extracting the precipitated oil by means of ether. The ethereal solution is dried and evaporated, when an oil remains which, in contact with cold hydrochloric acid or chloroform, soon solidifies. It is purified by dissolving in ethyl acetate and then cautiously adding light petroleum (90—110°), and separates as a sandy powder melting at 173°:

0·1130 gave 0·2544 CO_2 and 0·0500 H_2O. C = 61·4; H = 4·9.
0·1230 ,, 11·0 c.c. N_2 at 14° and 762 mm. N = 10·5.
$C_{14}H_{12}O_4N_2$ requires C = 61·8; H = 4·4; N = 10·3 per cent.

The acid is sparingly soluble in chloroform or benzene, and almost insoluble in light petroleum, but dissolves readily in acetone, ethyl acetate or alcohol.

The basicity was controlled by titrating with *N*/10-sodium hydroxide:

0·1040 neutralised 0·0296 NaOH, whereas the same weight of a dibasic acid, $C_{14}H_{12}O_4N_2$ requires 0·0305 NaOH.

Its *silver* salt was also analysed:

0·3006 gave 0·1314 Ag. Ag = 43·8.
$C_{14}H_{12}O_4N_2$ requires Ag = 44·4 per cent.

a-Cyano-β-styryl-β-methylacrylic Acid,
$C_6H_5 \cdot CH{:}CH \cdot CMe{:}C(CN) \cdot CO_2H$.

This substance was prepared by suspending ethyl sodiocyanoacetate, obtained from sodium (5·8 grams) and ethyl cyanoacetate (28 grams), in hot alcohol, mixing this with a solution of benzylideneacetone (36 grams) in alcohol, and heating on the water-bath for an hour. At the end of this time a yellow solid separated, which dissolved on adding water. This solution of the sodium derivative was decomposed by adding dilute hydrochloric acid, and the oil which was precipitated was extracted with ether, the ethereal solution washed until free from alcohol, and shaken with aqueous sodium carbonate solution.

The products remaining in the ether consisted of high-boiling oils, which proved difficult to separate. The main product was found in the sodium carbonate solution, and consisted of an acid which was precipitated as an oil on acidifying the solution. This was dissolved in ether, and the solution dried and evaporated, when the residue rapidly crystallised. The crystals were purified by dissolving in dilute methyl alcohol, from which the acid separated in minute, colourless needles melting at 188° to a red liquid.

A titration showed it to be monobasic:

0·2620 neutralised 0·0496 NaOH, whereas the same weight of a monobasic acid, $C_{13}H_{11}O_2N$, requires 0·0492 NaOH.

0·1277 gave 0·3420 CO_2 and 0·0600 H_2O. C = 73·0; H = 5·2.

$C_{13}H_{11}O_2N$ requires C = 73·2; H = 5·2 per cent.

The solution of the acid in concentrated sulphuric acid is colourless, and, on adding water, the substance is recovered unchanged.

a-Carboxyamino-β-styryl-β-methylacrylic Acid,
$C_6H_5 \cdot CH{:}CH \cdot CMe{:}C(CO \cdot NH_2) \cdot CO_2H$.

In order to prepare this substance, α-cyano-β-styryl-β-methylacrylic acid is dissolved in aqueous potassium hydroxide (40 per cent.), and the solution boiled for a few minutes, when the contents of the vessel suddenly become solid. Water and ice are then added, and the mass is acidified; the acid is collected and recrystallised from benzene, from which it separates in slender, colourless plates melting at 166°:

0·1180 gave 0·2925 CO_2 and 0·0640 H_2O. C = 67·5; H = 6·0.

0·1210 ,, 6·7 c.c. N_2 at 19° and 766 mm. N = 6·3.

$C_{13}H_{13}O_3N$ requires C = 67·5; H = 5·6; N = 6·1 per cent.

β-Styryl-β-methylacrylic Acid, $C_6H_5 \cdot CH{:}CH \cdot CMe{:}CH \cdot CO_2H$.

The amide just described passes readily into the above monobasic acid on digesting with dilute hydrochloric acid for an hour. The aqueous solution, on cooling, deposits a crop of crystals which, on recrystallisation from water, separate in beautiful, colourless plates melting at 190°:

0·1057 gave 0·2950 CO_2 and 0·0630 H_2O. C = 76·1; H = 6·6.

$C_{12}H_{12}O_2$ requires C = 76·6; H = 6·4 per cent.

A titration with *N*/10-sodium hydroxide gave the following result:

0·0850 required 0·0184 NaOH, whereas the same weight of a monobasic acid, $C_{12}H_{12}O_2$, requires 0·0181 NaOH.

β-Styryl-β-methylacrylic acid dissolves in most organic solvents, and its sodium salt in solution is unstable towards permanganate. It combines with bromine in the manner of unsaturated substances containing conjugated double bonds, forming an unsaturated *dibromide*.

αδ-Dicyano-βγ-diphenyl-Δ^β-butene-αδ-dicarboxylic Acid,

$CO_2H{\cdot}CH(CN){\cdot}CPh{:}CPh{\cdot}CH(CN){\cdot}CO_2H$.

This substance was prepared as follows: Sodium (5·7 grams), dissolved in ethyl alcohol, was mixed with ethyl cyanoacetate (28 grams), and, after the separation of the white sodium derivative, a solution of benzoin (26·5 grams) in hot alcohol was added with frequent shaking. The white sodium derivative immediately dissolved, yielding a deep yellow solution which, on heating for half an hour, deposited a bulky sodium derivative. The product was cooled, dissolved in water, acidified with hydrochloric acid, and extracted with ether. The extract was washed several times with water, and afterwards with sodium carbonate, which dissolves the chief product of the reaction. This solution was acidified with mineral acid, and a solid acid separated, which was collected and recrystallised from benzene, from which solvent it separated in colourless needles melting and decomposing at 136°:

0·1655 gave 0·4195 CO_2 and 0·0590 H_2O. C = 69·2; H = 4·0.

0·1675 „ 11·2 c.c. N_2 at 13° and 758 mm. N = 7·9.

$C_{20}H_{14}O_4N_2$ requires C = 69·4; H = 4·0; N = 8·1 per cent.

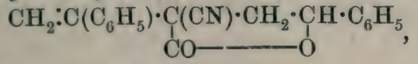
To determine its basicity, the acid was titrated with *N*/10-sodium hydroxide:

0·3565 neutralised 0·0831 NaOH, whereas the same weight of a dibasic acid, $C_{20}H_{14}O_4N_2$, requires 0·0825 NaOH.

The *sodium*, and especially the *potassium*, salt of the acid are very sparingly soluble in cold water. Consequently the acid does not dissolve readily in cold concentrated potassium hydroxide solution.

The acid is recovered unchanged after boiling with concentrated potassium hydroxide or hydrochloric acid.

Lactone of *γ-Cyano-ε-hydroxy-βε-diphenyl-*Δ^{α}*-pentene-γ-carboxylic Acid*,



$$\begin{array}{l} CH_2{:}C(C_6H_5)\cdot \underset{|}{C}(CN)\cdot CH_2\cdot \underset{|}{C}H\cdot C_6H_5, \\ \qquad\qquad\qquad\quad CO\text{————}O \end{array}$$

and *γ-Cyano-βε-diphenyl-*$\Delta^{\beta\delta}$*-pentadiene*,

$C_6H_5\cdot CMe{:}C(CN)\cdot CH{:}CH\cdot C_6H_5$.

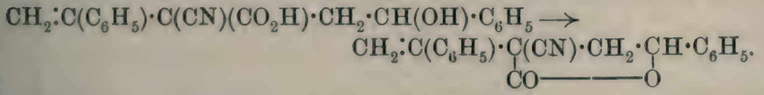
Acetophenone (24 grams) was added to the sodium derivative of ethyl cyanoacetate, prepared from sodium (4·6 grams) dissolved in alcohol and ethyl cyanoacetate (22·6 grams); the white sodium derivative disappeared after warming on the water-bath for fifteen minutes, and at the end of two hours a bulky sodium derivative separated, the contents of the flask becoming almost solid on cooling. This solid dissolved on adding water, and on acidifying the solution an oil was deposited, which was extracted with ether (*B*), the extract washed well with water to remove alcohol, and then shaken with dilute sodium carbonate solution. The sodium carbonate extract on acidifying yielded an oil, which was dissolved in ether, and the ethereal solution dried and evaporated.

During the process of drying, a quantity of crystals separated from the ethereal solution, but these proved to be the same substance as was obtained from the remainder of the solution after evaporation, when the oil which was first obtained rapidly crystallised on cooling.

The solid was drained on porous porcelain, and recrystallised from methyl alcohol, from which solvent it separated in large prisms of a beautiful pale green colour and melting at 157°:

0·1745 gave 0·5040 CO_2 and 0·0800 H_2O. C = 78·8; H = 5·1.
0·2754 „ 10·3 c.c. N_2 at 18° and 758 mm. N = 4·3.
$C_{19}H_{15}O_2N$ requires C = 78·9; H = 5·2; N = 4·8 per cent.

Although originally soluble in sodium carbonate, this substance was now insoluble in dilute alkalis even on warming, and must therefore have changed from an acid into a lactone (see Introduction):



$$\begin{array}{l} CH_2{:}C(C_6H_5)\cdot C(CN)(CO_2H)\cdot CH_2\cdot CH(OH)\cdot C_6H_5 \longrightarrow \\ \qquad\qquad\qquad\qquad CH_2{:}C(C_6H_5)\cdot \underset{|}{C}(CN)\cdot CH_2\cdot \underset{|}{C}H\cdot C_6H_5. \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CO\text{————}O \end{array}$$

The *lactone* of *γ-cyano-ε-hydroxy-βε-diphenyl-*Δ^{α}*-pentene-γ-carboxylic acid* dissolves in a methyl-alcoholic solution of potassium hydroxide on warming, and yields a clear solution on the addition of water. If this is acidified, a yellow precipitate of the hydroxy-acid first separates, but this rapidly passes into the lactone. Several attempts were made to isolate this hydroxy-acid, and this was found possible by acidifying the sodium carbonate extract mentioned above with acetic acid instead of with mineral acid.

The oily residue after extraction was placed in an evacuated desiccator containing solid potassium hydroxide, and after some days crystals appeared, which, however, were difficult to purify. They dissolved readily in cold sodium carbonate solution, but in contact with methyl or ethyl alcohol and several other solvents, the substance changed immediately into the sparingly soluble lactone. From a mixture of benzene and light petroleum, however, a specimen was obtained which melted about 120°, and this gave on analysis numbers which agreed approximately with those required for the hydroxy-acid.

The ethereal solution, *B* (p. 487), was dried, evaporated, and the residue on fractionation yielded a quantity of unchanged acetophenone and a small amount of neutral oil distilling at 200—230°/13 mm., which had a strong odour of nitrile.

This fraction was separated into two portions on redistillation, namely:

I. B. p. 210°/13 mm.; II. B. p. 225°/13 mm.; and these yielded on analysis the following results:

I. 0·1824 gave 0·5746 CO_2 and 0·106 H_2O. C = 86·0; H = 6·4.
0·1330 „ 6·3 c.c. N_2 at 16° and 768 mm. N = 5·6.
$C_{18}H_{15}N$ requires C = 88·2; H = 6·1; N = 5·7 per cent.
II. 0·1852 gave 0·5590 CO_2 and 0·1060 H_2O. C = 82·3; H = 6·4.
$C_{18}H_{17}ON$ requires C = 82·1; H = 6·5 per cent.

The latter substance, II, has the constitution

$$C_6H_5\cdot CMe{:}C(CN)\cdot CH_2\cdot CH(OH)\cdot C_6H_5,$$

and is therefore *γ-cyano-ε-hydroxy-βε-diphenyl-Δ^{β}-pentene*; it is doubtless the process of condensation by the elimination of carbon dioxide from the hydroxy-acid (see above).

The analytical results obtained in the case of substance I indicate that it has the constitution $C_6H_5\cdot CMe{:}C\cdot(CN)\cdot CH{:}CH\cdot C_6H_5$, and is *γ-cyano-βε-diphenyl-Δ^{β}-pentadiene.*

The above view of the constitution and of the method of formation of the two nitriles, I and II, has been verified by digesting the lactone (m. p. 157°) for eight hours with a concentrated solution of potassium hydroxide or barium hydroxide. Under these conditions the lactone loses carbon dioxide and passes chiefly into a neutral oil boiling at 225°/20 mm., from which by repeated fractionation the nitriles I and II were separated.

The stability of these nitriles towards ordinary hydrolytic reagents is very remarkable, for after prolonged digestion with concentrated potassium hydroxide no trace of an acid could be isolated, and even when the most concentrated barium hydroxide solution was employed, only a very small proportion of an acid was produced; this was obtained in the form of colourless needles melting at 130°.

The author desires to express his indebtedness to Prof. W. H. Perkin for the interest he has taken in this work, and also to the Chemical Society for a grant which has defrayed part of the expense of this investigation.

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LXII.—*The Action of Fuming Sulphuric Acid on Triphenylsilicol.*

By FREDERIC STANLEY KIPPING and GEOFFREY MARTIN.

SOME years ago Kipping and Lloyd attempted to obtain a sulphonic derivative of tetraphenylsilicane, and also examined, although not very thoroughly, the behaviour of triphenylsilicol towards various sulphonating agents (Trans., 1901, **79**, 449). In all of these experiments, many of which were carried out below 0°, the only organic products which were isolated were found to be sulphonic derivatives of benzene.

In the course of more recent work (Kipping, Trans., 1907, **91**, 209, 717), it was found that, whereas silico-hydrocarbons, which contain the benzyl group, such as benzylmethylethylpropylsilicane, $SiMeEtPr{\cdot}C_7H_7$, may be directly transformed into the corresponding sulphonic acids with the aid of sulphuric acid or chlorosulphonic acid, yet when silico-hydrocarbons containing a phenyl group are treated with sulphonating agents, this group is eliminated as benzene or benzenesulphonic acid. Thus, when phenylbenzylethylpropylsilicane, $SiEtPrPh{\cdot}CH_2{\cdot}C_6H_5$, is warmed with sulphuric acid, it gives benzene and a sulphonic compound of the constitution $(SiEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H)_2O$.

On the appearance recently of a paper by Ladenburg (*Ber.*, 1907, **40**, 2274), in which he claims to have prepared a sulphonic derivative of triphenylsilicol, we tried to prepare this compound according to the meagre instructions contained in his communication. Instead of obtaining a sulphonic derivative of the silicol, however, we only succeeded in isolating benzenedisulphonic acid mixed, probably, with a little benzenemonosulphonic acid.

These results were communicated to Ladenburg by one of us, and at the same time it was suggested that the evidence for the existence of the trisulphonic acid of triphenylsilicol, which he had published, was unsatisfactory, since the results of the analysis of the barium salt prepared by him agreed almost as well with those required for the barium salt of benzenesulphonic acid. A request was also made for details as to the conditions under which he obtained his "triphenylsilicoltrisulphonic acid," especially as regards the temperature and the strength of the fuming sulphuric acid used; but the only information received in reply was that it was "zweckmässig" to work in the cold.

Even in his later communication (*Ber.*, 1908, **41**, 966), in which he admits the formation of benzenesulphonic acid, Ladenburg does not give any account of the conditions of his experiment, nor any description of the separation and purification of the supposed silicon compound, nor any account of its properties. He merely states that the specimen of the barium salt which he analysed contained 3·3 per cent. of silicon, and "war annähernd rein"; but as the calculated percentage of silicon is 3·9, his own analyses allow for impurity amounting to more than 15 per cent. With regard to this analysis, the further question arises, was the silicon in the specimen really present in the form of triphenylsilicoltrisulphonic acid?

To this question Ladenburg's published statements afford no answer.

As we have repeatedly tried to prepare triphenylsilicoltrisulphonic acid, and to isolate it in the form of a pure salt, and have invariably been unsuccessful, we are forced to the conclusion that even if this compound is formed in appreciable proportion by the method described by Ladenburg, practically the whole of the silicol undergoes decomposition, with formation of benzene mono- and di-sulphonic acids, and other products. When the sulphonation is carried out at low temperatures, a small proportion of some sulphonic acid which contains silicon, possibly the compound $SiO(C_6H_4{\cdot}SO_3H)_2$, seems to be produced, but we have been unable to isolate any pure crystalline salt of this or of any other sulphonic acid containing silicon. Until, therefore, a pure specimen of triphenylsilicoltrisulphonic acid, or of one of its derivatives, is obtained, it is hardly necessary to include this compound among the known organic derivatives of silicon.

EXPERIMENTAL.

In our first experiments, 3 grams of finely powdered triphenylsilicol, $Si(C_6H_5)_3{\cdot}OH$, were gradually added to 18 grams of fuming sulphuric acid (containing 20 per cent. of sulphur trioxide) at the ordinary temperature.

In agreement with Ladenburg's statement, the substance dissolved easily with evolution of heat, colouring the acid brown, but after a few minutes there separated at the bottom of the vessel some gelatinous silicic acid, containing a small amount of organic matter.

The solution was poured into cold water, filtered, neutralised with barium carbonate, and again filtered. The barium salt, obtained in white scales on evaporating to a small bulk, was converted into the ammonium salt by treating its aqueous solution with excess of ammonium carbonate, filtering, and heating until all the ammonium carbonate was expelled; the residue was then recrystallised from methyl alcohol. The ammonium salt thus obtained was dried at 100° and analysed, with the following results:

0·5471 gave 0·0045 SiO_2. $Si = 0·4$.
0·6838 „ 0·0820 NH_3. $N = 9·9$.
$Si(C_6H_4 \cdot SO_3 \cdot NH_4)_3 \cdot OH$ requires $Si = 5$; $N = 7·4$ per cent.

The percentage of nitrogen lies between that required for $C_6H_4(SO_3 \cdot NH_4)_2$ ($N = 10·3$) and $C_6H_5 \cdot SO_3 \cdot NH_4$ ($N = 8·0$). The salt was in all probability a mixture of these two compounds containing small quantities of silicon sulphonic derivatives of unknown composition.

As at the ordinary temperature a large proportion of the silicon in the triphenylsilicol is eliminated as silica, we next studied the result of sulphonating at lower temperatures.

Pure finely powdered triphenylsilicol (3 grams) was added in very small quantities at a time to fuming sulphuric acid (20 per cent. of sulphur trioxide: 18 grams). The acid was kept at 0° during the whole course of the experiment, and the silicol was added so slowly that the operation took two hours. Nevertheless, although the silicol readily dissolved at first, after some time a white solid appeared in the liquid. This solid was insoluble in water or alcohol, and when heated with sulphuric acid, it only blackened to a slight extent, leaving a large residue of silica.

The concentrated acid, containing the dissolved triphenylsilicol, was gradually poured on ice, when, although the temperature fell below 0°, a cloud of gelatinous silicic acid containing some organic matter appeared in the liquid and was separated by filtration. The acid was then neutralised with barium carbonate, the solution filtered, and the filtrate treated with excess of ammonium carbonate; after separating the barium carbonate, the solution was evaporated on the water-bath until the excess of ammonium carbonate was expelled. The crude ammonium salt thus obtained solidified on cooling to a hard mass, and the silicon in a portion of the dried solid was estimated:

0·2753 gave 0·0245 SiO_2. $Si = 4·2$.

The purity of the silica was established by evaporating with hydrofluoric acid, when practically the whole disappeared.

The fact that this crude ammonium salt contains approximately the same percentage of silicon as that required for ammonium triphenylsilicolsulphonate is, of course, no proof of the presence of the latter, and, as shown below, this crude preparation contains a considerable proportion of ammonium benzenedisulphonate.

In order to separate the components of this crude ammonium salt, it was dissolved in water, and the neutral solution precipitated with *l*-menthylamine hydrochloride. The precipitate thus obtained was repeatedly crystallised from moist ethyl acetate, and was thus separated into two portions, one soluble in ethyl acetate and the other insoluble. The substance soluble in ethyl acetate was recrystallised several times from this solvent, and was then obtained in colourless prisms melting at 212°. Silicon could not be detected in the pure sample, and a combustion gave the following results:

0·1364 gave 0·2855 CO_2 and 0·1083 H_2O. C = 57·1; H = 8·8.

$C_6H_4(SO_3H)_2,(C_{10}H_{21}N)_2$ requires C = 56·9; H = 8·8 per cent.

The salt therefore is l-*menthylamine benzenedisulphonate*; it is insoluble in ether, but very soluble in ethyl acetate, alcohol, or hot water.

The portion insoluble in ethyl acetate was a sticky, brown mass, soluble in methyl alcohol, and sparingly soluble in chloroform, but insoluble or nearly so in ether or water. It was repeatedly washed with warm ethyl acetate in order to extract any menthylamine benzenedisulphonate, and then dissolved in methyl alcohol and precipitated with ethyl acetate; finally the soft, white mass was dried at 100° until constant. It then formed a brittle, vitreous, colourless solid, which softened above 200°, and frothed up and decomposed between 250—260°.

An analysis of the substance gave the following results:

0·1544 gave 0·3008 CO_2 and 0·1064 H_2O. C = 53·1; H = 7·6.

0·2578 ,, 0·0323 SiO_2. Si = 5·9.

A second sample of this substance was obtained in a later experiment, in which 11 grams of triphenylsilicol were sulphonated in a similar manner. The dried preparation gave on analysis the following results:

0·2436 gave 0·4825 CO_2, 0·1634 H_2O, and 0·0294 SiO_2. C = 54·0; H = 7·5; Si = 5·7.

0·1509 gave 0·2981 CO_2 and 0·1019 H_2O. C = 53·9; H = 7·5.

These values do not agree at all with those required for the menthylamine salt of triphenylsilicoltrisulphonic acid (C = 58·6; H = 8·1; Si = 2·9 per cent.), and although the two samples which were analysed were very similar in composition, their behaviour seemed to indicate that they were mixtures.

In later experiments, sulphonation was carried out at much lower temperatures, namely, at about −10°; under these conditions very little, if any, separation of silica occurred during the process, but a small quantity of a gelatinous precipitate was produced on pouring the acid solution on ice; this precipitate consisted principally of triphenylsilicol. The sulphonation product was converted into the ammonium salt as before, and the dry ammonium salt was extracted with boiling ethyl acetate containing a very little methyl alcohol. The extract on cooling deposited colourless, lustrous crystals, which were dissolved in water, and the solution was treated with *l*-menthylamine hydrochloride. The precipitate thus obtained, after recrystallising from water, consisted of pure *l*-menthylamine benzenesulphonate:

0·1939 gave 0·4348 CO_2 and 0·1540 H_2O. $C=61·2$; $H=8·8$.
$C_6H_5·SO_3H,C_{10}H_{21}N$ requires $C=61·3$; $H=8·7$ per cent.

l-*Menthylamine benzenesulphonate* separates from water in colourless needles, which melt at 223—226° and are readily soluble in water, chloroform, or methyl alcohol, sparingly so in ethyl acetate, and insoluble in ether.

The formation of the mono- instead of the di-sulphonic acid in this experiment is doubtless owing to the lower temperature at which sulphonation was carried out. The quantity of this salt corresponded with 47 per cent. of the silicol if the latter was partly decomposed, and with 16 per cent. if it was completely decomposed.

The crude ammonium salt from which the ammonium benzenesulphonate had been extracted with ethyl acetate was treated with methyl alcohol; a small proportion remained undissolved; both portions contained combined silicon. The methyl-alcoholic solution gave on evaporation a residue which did not crystallise, and which was precipitated with excess of *l*-menthylamine hydrochloride; from this precipitate a further quantity of crystalline menthylamine benzenemonosulphonate was isolated; but the remainder of the menthylamine salt, although it separated in crystals from a saturated solution of menthylamine hydrochloride, became oily when washed with water to free it from the hydrochloride. This oil was much more soluble in the presence of menthylamine hydrochloride than in pure water, and seemed to be a product of hydrolysis of some normal menthylamine salt; as it could not be obtained in crystals it was not further examined, but it was probably similar in composition to the vitreous solid described above.

The ammonium salt insoluble in methyl alcohol was also converted into the menthylamine salt; this compound was deposited in an oily condition from a mixture of methyl alcohol and ethyl acetate, and when dried at 100° it formed a colourless, vitreous solid, which could not be obtained in crystals:

0·2258 gave 0·4636 CO_2 and 0·1577 H_2O. C=56·0; H=7·8.
0·2311 „ 0·0243 SiO_2. Si=4·9.
$SiO(C_6H_4{\cdot}SO_3H,C_{10}H_{21}N)_2$ requires C=57·5; H=7·8; Si=4·25 per cent.

From these results we may presume that this and the other preparations containing silicon which were analysed were possibly mixtures of the normal menthylamine salt of diphenylsiliconedisulphonic acid and the corresponding menthylamine hydrogen salt.

From 4·5 grams of silicol sulphonated at −10° we obtained about 1·6 grams of menthylamine salts containing silicon, and 2·4 grams of pure menthylamine benzenemonosulphonate.

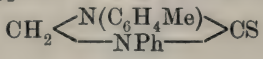
University College,
Nottingham.

LXIII.—*Thiotetrahydroquinazolines, Methylenecarbamides, Dicarbanilinomethylenediamines and their Homologues.*

By Alfred Senier and Frederick George Shepheard.

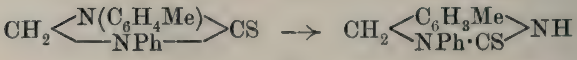
The interaction of arylthiocarbimides with arylmethylenediamines at temperatures of 150° to 200° results in the formation of cyclic compounds, cyclic carbamides and quinazolines. When the para-position in the aryl group of either the diamine or the thiocarbimide or both of them is occupied, thiotetrahydroquinazoline derivatives and a diarylthiocarbimide are formed. Thus, in the instance of di-*p*-tolylmethylenediamine and phenylthiocarbimide, the stages of the reaction may be explained:

$$CH_2(NH{\cdot}C_6H_4Me)_2 + Ph{\cdot}NCS = Ph{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me +$$



$$CH_2{<}\begin{matrix}N(C_6H_4Me)\\ NPh\end{matrix}{>}CS$$

(I.)

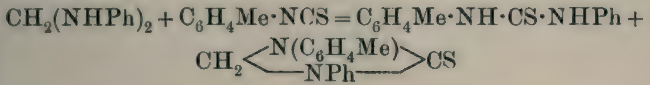


$$CH_2{<}\begin{matrix}N(C_6H_4Me)\\ NPh\end{matrix}{>}CS \longrightarrow CH_2{<}\begin{matrix}C_6H_3Me\\ NPh{\cdot}CS\end{matrix}{>}NH$$

(II.)

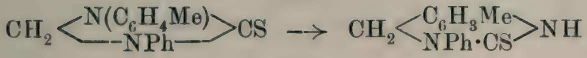
The same quinazoline is obtained whether an alkyl group occupies the para-position in the diamine or in the thiocarbimide; this is shown in sections 4 and 8 (pp. 499, 502).

The following equations corresponding with those given above show that this might be expected:



$$CH_2(NHPh)_2 + C_6H_4Me{\cdot}NCS = C_6H_4Me{\cdot}NH{\cdot}CS{\cdot}NHPh + CH_2\left<\begin{matrix}N(C_6H_4Me)\\NPh\end{matrix}\right>CS$$

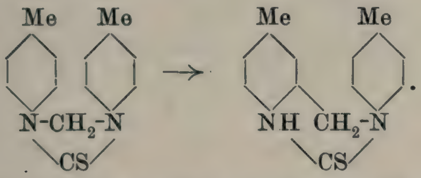
(I.)



$$CH_2\left<\begin{matrix}N(C_6H_4Me)\\NPh\end{matrix}\right>CS \longrightarrow CH_2\left<\begin{matrix}C_6H_3Me\\NPh{\cdot}CS\end{matrix}\right>NH$$

(II.)

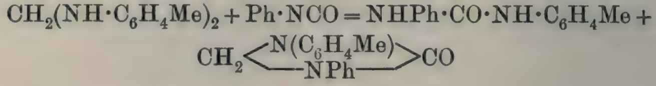
The metastatic rearrangement shown in the second equation is similar to the methylenebenzidine metastasis of Eberhardt and Welter (Senier and Compton, Trans., 1907, **91**, 1928). As will be seen from the following diagram, however, the change takes place in one ring only, and this is true whether the para-position is occupied by an alkyl group in one ring, or, as shown in the diagram, in both rings:



By a modification of the above equations it may easily be shown that the condensation of methyleneaniline and *p*-tolylthiocarbimide should give the same tetrahydroquinazoline as that derived from diphenylmethylenediamine and *p*-tolylthiocarbimide. The experiment described in section 13 (p. 505) shows that this is true.

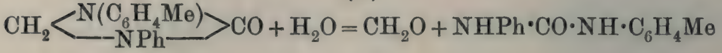
The quinazolines were identified by comparing their properties with the nearly related derivatives described by previous investigators (Busch, *Ber.*, 1892, **25**, 2853; Paal and Commerell, *Ber.*, 1894, **27**, 1866, 2427). These compounds are characteristically difficult to desulphurise; with sodium and ethyl alcohol there is very little action, and even when treated with a large excess of sodium in hot amyl-alcoholic solution they still retain a considerable proportion of sulphur.

In all instances of higher temperature experiments in which thiocarbimides react with methylenediamines containing free para-positions, and in all cases where the thiocarbimides are replaced by carbimides, unstable cyclic methylene-carbamides or -thiocarbamides are probably formed associated with a diaryl-carbamide or -thiocarbamide. The instability of the cyclic methylene-carbamides or -thiocarbimides is due to the extreme readiness with which they admit of hydrolysis, yielding formaldehyde and diarylcarbamides, which products were identified in each experiment. These reactions may be explained by the following equations in the case of phenylcarbimide and di-*p*-tolylmethylenediamine:



$$CH_2(NH{\cdot}C_6H_4Me)_2 + Ph{\cdot}NCO = NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me + CH_2{<}\substack{N(C_6H_4Me)\\NPh}{>}CO$$

(I.)



$$CH_2{<}\substack{N(C_6H_4Me)\\NPh}{>}CO + H_2O = CH_2O + NHPh{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$$

(II.)

That these hydrolytically unstable cyclic carbamides are actually formed as intermediate compounds is rendered extremely probable by the fact that in two instances, (11) and (12), employing a different reaction, in which methyleneaniline is substituted for a methylenediamine, we succeeded in isolating them and proved their extreme susceptibility to hydrolysis.

At the ordinary temperature the course of the reactions is in agreement with previous experiments; carbanilino- or thiocarbanilinomethylenediamines or their homologues are always formed (Senier and Goodwin, Trans., 1901, **79**, 254; 1902, **81**, 283).

1. *Diphenylmethylenediamine and Phenylcarbimide.*

Dicarbanilinodiphenylmethylenediamine, $CH_2(NPh{\cdot}CO{\cdot}NHPh)_2$.—Diphenylmethylenediamine, dried in a vacuum over phosphoric oxide (1 mol.), was dissolved in dry benzene or dry ether, phenylcarbimide (2 mols.) was added, and the mixture kept for some time in a well-corked flask at the ordinary temperature. Small, colourless needles soon began to separate, the separation being complete in the course of a few hours, when they were collected and washed with dry benzene or dry ether. The compound melts and decomposes at 222° (corr.); it is almost insoluble in benzene or light petroleum, but dissolves more readily in ether or chloroform, and easily in alcohol, glacial acetic acid, ethyl acetate, or acetone:

0·1916 gave 0·5198 CO_2 and 0·1090 H_2O. $C = 74{\cdot}01$; $H = 6{\cdot}36$.
0·1615 ,, 18·5 c.c. N_2 (moist) at 18° and 746 mm. $N = 12{\cdot}98$.
$C_{27}H_{24}O_2N_4$ requires $C = 74{\cdot}31$; $H = 5{\cdot}50$; $N = 12{\cdot}84$ per cent.

The decomposition of this compound just above its melting point is attended by the liberation of aniline, detected by the bleaching-powder reaction, and of a distinct *iso*nitrile odour; from the residue, carbanilide was isolated. Dicarbanilinodiphenylmethylenediamine is very easily hydrolysed into formaldehyde and carbanilide; the least trace of moisture in a solvent used to dissolve it causes hydrolysis on warming, thus:

$$CH_2(NPh{\cdot}CO{\cdot}NHPh)_2 = CH_2O + 2CO(NHPh)_2.$$

Rimini's test (*Amer. Chem. J.*, 1900, 22, 132) was used for the detection of the formaldehyde, which gives a blue colour, quickly changing to green and red by treatment with solutions of suitable strength of phenylhydrazine hydrochloride, sodium nitroprusside, and sodium hydroxide.

An attempt was made to prepare a monocarbanilino-derivative by employing half the proportion of phenylcarbimide, but the dicarbanilinodiamine only was formed.

The high temperature experiment was conducted in a flask, from which moisture was excluded by a drying-tube. The closed tube employed in the experiments of Senier and Goodwin was found unnecessary. The methylenediamine and phenylcarbimide, in the proportions given above, were placed in a flask, and heated in an oil-bath for about twenty minutes at a temperature rising to 130°. The clear liquid at first formed became viscid and finally solid. On treatment with cold alcohol, about half dissolved, and the soluble portion on examination proved to be carbanilide; no trace of dicarbanilino-compound was isolated, nor did the alcoholic solution contain formaldehyde, showing that the formation of carbanilide was not due to the hydrolysis of any dicarbanilino-compound. From the residue insoluble in alcohol we were unable to isolate a definite compound. The residue, however, when warmed with alcohol and dilute hydrochloric acid, was readily hydrolysed into carbanilide and formaldehyde. At the higher temperature, then, dicarbanilinodiphenylmethylenediamine is not formed, but, instead, carbanilide and a methylenecarbamide, which we were unable to isolate, but which is indicated by its products of hydrolysis, carbanilide and formaldehyde.

2. *Diphenylmethylenediamine and α-Naphthylcarbimide.*

Dicarbonaphthylaminodiphenylmethylenediamine,
$CH_2(NPh\cdot CO\cdot NH\cdot C_{10}H_7)_2$.
—At the ordinary temperature, diphenylmethylenediamine (1 mol.) and α-naphthylcarbimide (2 mols.) interact, colourless, microscopic needles separating from the solution in ether or benzene. These darken at 218°, and melt and decompose at about 229° (corr.). *Dicarbonaphthylaminodiphenylmethylenediamine* is almost insoluble in benzene or light petroleum, more soluble in ether or chloroform, but dissolves easily in alcohol, glacial acetic acid, ethyl acetate, or acetone:

0·2017 gave 18·6 c.c. N_2 (moist) at 20° and 774 mm. N = 10·77.
$C_{35}H_{28}O_2N_4$ requires N = 10·45 per cent.

This compound is very readily hydrolysed, giving formaldehyde, recognised by Rimini's test, and crystals of *s*-phenyl-*a*-naphthylcarbamide, which melt at 222—223°.

An experiment at a higher temperature (150°) gave a product from which it was found impossible to isolate any definite compound except the above-mentioned phenyl-*a*-naphthylcarbamide.

3. *Diphenylmethylenediamine and Phenylthiocarbimide.*

The thiocarbimides react with the methylenediamines much less readily than the analogous carbimides. At low temperatures in solution after keeping for several weeks, a small yield of dithiocarboarylaminomethylenediamine is obtained, whilst at higher temperatures no definite compounds appear to be formed unless an aryl group in either the diamine or the carbimide contains a para-substituent. When this is the case, derived quinazolines are formed.

Dithiocarbanilinodiphenylmethylenediamine, $CH_2(NPh{\cdot}CS{\cdot}NHPh)_2$.—Diphenylmethylenediamine (1 mol.), dissolved in dry ether or dry benzene, was treated with phenylthiocarbimide (2 mols.) at the ordinary temperature, and set aside for from three to six weeks. At temperatures above 30°, a more vigorous action takes place, but its character changes; in an experiment in which the temperature was allowed to rise nearly to the boiling point of the benzene used as a solvent, an abundant crop of crystals of thiocarbanilide separated on cooling.

Dithiocarbanilinodiphenylmethylenediamine crystallises in prisms, which melt at 141—142° (corr.); it dissolves readily in alcohol, chloroform, or glacial acetic acid, less so in ether, light petroleum, or benzene:

0·1495 gave 0·3777 CO_2 and 0·0724 H_2O. $C = 68·90$; $H = 5·29$.

$C_{27}H_{24}N_4S_2$ requires $C = 69·18$; $H = 5·17$ per cent.

If a solution of this compound in rectified spirit is warmed for a few minutes, its hydrolysis is complete.

At higher temperatures (150°) this reaction results in a hard, glassy product. This was separated into two portions by treatment with cold benzene. The insoluble residue consisted chiefly of thiocarbanilide. From the solution, on the addition of light petroleum, a precipitate was obtained from which no definite compound could be isolated, but the latter was readily hydrolysed, giving thiocarbanilide and formaldehyde.

4. *Diphenylmethylenediamine and* p-*Tolylthiocarbimide.*

Dithiocarbo-p-*toluidinodiphenylmethylenediamine*,

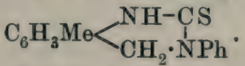
$CH_2(NPh{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me)_2$.

—This compound is obtained from ethereal solution in colourless crystals, which melt at 140—141° (corr.):

0·2175 gave 21·6 c.c. N_2 (moist) at 16° and 756 mm. N = 11·52
0·1551 „ 0·1475 $BaSO_4$. S = 13·06.
$C_{29}H_{28}N_4S_2$ requires N = 11·29; S = 12·92 per cent.

When dithiocarbo-*p*-toluidinodiphenylmethylenediamine is heated above its melting point, hydrogen sulphide is evolved. Hydrolysis with the formation of *s*-phenyl-*p*-tolylthiocarbamide and formaldehyde may be brought about by warming with dilute acids or with rectified spirit; prolonged boiling with acids effects the decomposition of the thiocarbamide with evolution of thiocarbimide.

3-*Phenyl*-6-*methyl*-2-*thio*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



$$C_6H_3Me\lt\begin{matrix}NH-CS\\ |\\ CH_2{\cdot}NPh\end{matrix}.$$

—At high temperatures (200°), the heating being continued for three hours, a crystalline distillate of *s*-phenyl-*p*-tolylthiocarbamide collected in the cooler parts of the apparatus, and the residue solidified on cooling to a mass of nearly colourless crystals. Neither the distillate nor the residue gave any evidence of formaldehyde on treatment with dilute acids, showing that the reaction at the higher temperature is different from that which occurs at the lower temperature; no trace of the compound formed at the lower temperature could be detected.

The residue was recrystallised from alcohol several times until the melting point was constant. The compound, which for the reasons already given we regard as 3-*phenyl*-6-*methyl*-2-*thio*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, crystallises in brilliant plates or flat prisms which become slightly yellow above 236°, begin to melt at 242°, and melt completely at 250° (corr.):

0·1540 gave 0·3966 CO_2 and 0·0791 H_2O. C = 70·25; H = 5·75.
0·2266 „ 21·9 c.c. N_2 (moist) at 17° and 747 mm. N = 11·02.
0·1442 „ 0·1343 $BaSO_4$. S = 12·78.
$C_{15}H_{14}N_2S$ requires C = 70·82; H = 5·54; N = 11·03; S = 12·61 per cent.

This compound is almost insoluble in light petroleum, slightly soluble in alcohol or ether, more so in benzene or glacial acetic acid and dissolves readily in chloroform, acetone, or ethyl acetate. It also dissolves in hot concentrated hydrochloric acid, from which it separates unaltered on cooling. Concentrated solution of potassium hydroxide in water has no action on it. Replacement of the sulphur by hydrogen by treating the alcoholic solution of the base with sodium takes place very slowly; in amyl-alcoholic solution it is rather more rapid, but in any case large proportions of sodium are required.

Two platinichlorides were obtained:

Monoplatinichloride, $(C_{15}H_{14}N_2S)_2,H_2PtCl_6$.—A solution of chloroplatinic acid was added to a solution of the base in acetic acid, when this platinum salt separated as a light orange, amorphous powder:

0·1464 gave 0·0314 Pt. Pt = 21·44.

$C_{30}H_{30}N_4Cl_6S_2Pt$ requires Pt = 21·22 per cent.

Diplatinichloride, $C_{15}H_{14}N_2S,H_2PtCl_6$.—This compound was obtained as a dark orange, amorphous precipitate by adding a solution of chloroplatinic acid to a solution of the base in alcohol:

0·1786 gave 0·0521 Pt. Pt = 29·17.

$C_{15}H_{16}N_2Cl_6SPt$ requires Pt = 29·36 per cent.

5. *Diphenylmethylenediamine and* o-*Tolylthiocarbimide.*

*Dithiocarbo-*o*-toluidinodiphenylmethylenediamine*,

$CH_2(NPh\cdot CS\cdot NH\cdot C_6H_4Me)_2$.

—Colourless crystals of this unstable compound, which melted at 121—123°, separated from the solution in benzene or ether. Decomposition takes place at the ordinary temperature, and is more rapid on warming, with evolution of thiocarbimide:

0·1931 gave 19·9 c.c. N_2 (moist) at 17° and 761 mm. N = 11·98.
0·1262 ,, 0·1199 $BaSO_4$. S = 12·52.

$C_{29}H_{28}N_4S_2$ requires N = 11·29; S = 12·92 per cent.

The high percentage of nitrogen and the low percentage of sulphur found is doubtless due to the loss of thiocarbimide during the preparation. This compound dissolves sparingly in light petroleum or benzene, more readily in alcohol or ether, and easily in chloroform or glacial acetic acid. Hydrolysis takes place quickly when the compound is warmed with dilute acid.

At higher temperatures (200°) the course of the reaction was similar to that observed above (3), and the only compound we were able to isolate was *s*-phenyl-*o*-tolylthiocarbamide.

6. *Di-*p*-tolylmethylenediamine and Phenylcarbimide.*

*Dicarbanilinodi-*p*-tolylmethylenediamine*,

$CH_2[N(C_6H_4Me)\cdot CO\cdot NHPh]_2$.

—Di-*p*-tolylmethylenediamine, m. p. 85—86°, was prepared by Eberhardt and Welter's method (*Ber.*, 1894, **27**, 1808), and was treated with phenylcarbimide in the usual manner. Well-formed, colourless prisms were obtained, which, after recrystallisation from alcohol, melted at 171° (corr.):

0·2418 gave 0·6615 CO_2 and 0·1410 H_2O. C = 74·61; H = 6·52.
0·1850 ,, 18·6 c.c. N_2 (moist) at 18° and 768 mm. N = 11·74.
$C_{29}H_{28}O_2N_4$ requires C = 74·95; H = 6·07; N = 12·06 per cent.

*Dicarbanilinodi-*p*-tolylmethylenediamine* is slightly soluble in light petroleum or ether, more soluble in benzene, and readily so in other usual organic solvents. It is more stable than the other compounds of its class described in this paper. It may be recrystallised from warm rectified spirit without decomposition; if, however, a small proportion of acid is present, hydrolysis takes place with the evolution of formaldehyde and the formation of *s*-phenyl-*p*-tolylcarbamide. The carbamide was identified by analysis, by its melting point, and also by the absence of depression of the melting point in the case of a mixture of the compound with a specimen of the carbamide prepared in the ordinary way.

An attempt was made to prepare monocarbanilinodi-*p*-tolylmethylenediamine by bringing together at the ordinary temperature di-*p*-tolylmethylenediamine (1 mol.) and phenylcarbimide (1 mol.) in benzene solution. Crystals of *s*-phenyl-*p*-tolylcarbamide separated, and a further crop of crystals were obtained by the addition of light petroleum to the solution. No monocarbanilino-compound was formed, but after removal of the carbamide, on evaporation of the clear benzene solution to dryness, and treatment of the residue with warm alcohol, small needles were obtained which melted at 207—208°, and were identified as the isomeric methylene-*p*-toluidine of Eberhardt and Welter (*loc. cit.*); thus the monocarbanilino-compound, if formed at all, decomposes into *s*-phenyl-*p*-tolylcarbamide and methylene-*p*-toluidine.

An experiment at higher temperatures (160°) resulted in the formation of *s*-phenyl-*p*-tolylcarbamide, only slightly soluble in benzene, and in the benzene solution, an unstable compound, probably methylenephenyl-*p*-tolylcarbamide. The latter compound could not be isolated, but the products of its hydrolysis, formaldehyde and *s*-phenyl-*p*-tolylcarbamide, were identified.

7. *Di-*p*-tolylmethylenediamine and α-naphthylcarbimide.*

*Dicarbonaphthylaminodi-*p*-tolylmethylenediamine*,
$CH_2[N(C_6H_4Me)\cdot CO\cdot NH\cdot C_{10}H_7]_2$.
—The reaction at the ordinary temperature yielded, from benzene solution, needles which melted at 23·5—224·5° (corr.):

0·2280 gave 20·2 c.c. N_2 (moist) at 19° and 767·5 mm. N = 10·28.
$C_{37}H_{32}O_2N_4$ requires N = 9·93 per cent.

The above compound is very slightly soluble in ether, light petroleum, or benzene, but dissolves more easily in ethyl acetate, chloroform, or glacial acetic acid. It readily undergoes hydrolysis, giving formaldehyde and *s*-*p*-tolyl-*a*-naphthylcarbamide (see below).

Experiments were made at higher temperatures. As in other cases, the methylenecarbamide probably formed could not be isolated, but both products of its hydrolysis were identified.

s-p-*Tolyl-a-naphthylcarbamide*, $C_6H_4Me\cdot NH\cdot CO\cdot NH\cdot C_{10}H_7$.—This substance, which does not appear to have been previously described, was also prepared by the interaction of *a*-naphthylcarbimide and *p*-toluidine in ethereal solution. It crystallises in needles, which melt at 234° (corr.):

0·2248 gave 20·0 c.c. N_2 (moist) at 18·5° and 774 mm. N = 10·42.

$C_{18}H_{16}ON_2$ requires N = 10·15 per cent.

In most organic solvents this compound is readily soluble, but it is only sparingly soluble in light petroleum, chloroform, or ether.

8. *Di*-p-*tolylmethylenediamine and Phenylthiocarbimide.*

Dithiocarbanilinodi-p-*tolylmethylenediamine*,

$CH_2[N(C_6H_4Me)\cdot CS\cdot NHPh]_2$.

—The above compound is obtained at the ordinary temperature, and crystallises from its ethereal solution in small, colourless prisms, which melt and decompose at 225° (corr.):

0·2184 gave 0·5628 CO_2 and 0·1130 H_2O. C = 70·26; H = 5·79.

$C_{29}H_{28}N_4S_2$ requires C = 70·09; H = 5-68 per cent.

On hydrolysis this compound yields *s*-phenyl-*p*-tolylthiocarbamide and formaldehyde.

The condensation at a high temperature (200°) was conducted in the same manner as before. The course of the reaction and the products obtained were precisely the same as in the case of the interaction of diphenylmethylenediamine and *p*-tolylthiocarbimide (section 4): the distillate yielding *s*-phenyl-*p*-tolylthiocarbamide, and the residue, 3-phenyl-6-methyl-2-thio-1 : 2 : 3 : 4-tetrahydroquinazoline. This fact is referred to in the first part of this paper.

9. *Di*-p-*tolylmethylenediamine and* p-*Tolylthiocarbimide.*

Dithiocarbo-p-*toluidinodi*-p-*tolylmethylenediamine*,

$CH_2[N(C_6H_4Me)\cdot CS\cdot NH\cdot C_6H_4Me]_2$.

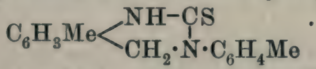
—The experiment at the ordinary temperature yields crystals melting at 174° (corr.):

0·1629 gave 0·4246 CO_2 and 0·0988 H_2O. C = 71·09; H = 6·78.

$C_{31}H_{32}N_4S_2$ requires C = 70·94; H = 6·15 per cent.

The above compound gives formaldehyde and *s*-di-*p*-tolylthiocarbamide when hydrolysed. The melting point of the latter (176°) is very near that of the former compound, and their percentage compositions are nearly the same, but the identity of the substituted diamine was established by its yielding formaldehyde on hydrolysis, and by the fact that the melting point of a mixture of this compound with a specimen of the carbamide showed a decided depression.

3-p-*Tolyl*-6-*methyl*-2-*thio*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



$$C_6H_3Me<\begin{matrix}NH-CS\\ \quad\ \ |\\ CH_2\cdot N\cdot C_6H_4Me\end{matrix}.$$

—The experiment at a higher temperature (200°) was conducted in the same manner as before (section 4). The crystalline distillate, after recrystallisation from alcohol, melted at 176° and proved to be s-di-*p*-tolylthiocarbamide. The residue was recrystallised from alcohol, dissolved in benzene, and filtered. Light petroleum was added, and, on keeping, colourless, glistening plates separated, which were collected and dried. The compound becomes yellow above 234°, softens at 255° and melts completely at 262° (corr.). It is slightly soluble in light petroleum, more so in alcohol or ether, and dissolves readily in benzene, chloroform, or ethyl acetate:

0·2199 gave 0·5781 CO_2 and 0·1195 H_2O. $C = 71·69$; $H = 6·08$.

$C_{16}H_{16}N_2S$ requires $C = 71·60$; $H = 6·01$ per cent.

10. *Di*-p-*tolylmethylenediamine and* o-*Tolylthiocarbimide.*

Dithiocarbo-o-*toluidinodi*-p-*tolylmethylenediamine*,

$$CH_2[N(C_6H_4Me)\cdot CS\cdot NH\cdot C_6H_4Me]_2.$$

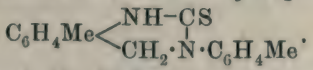
—From the experiment conducted at the ordinary temperature colourless needles were obtained which melt at 141° (corr.):

0·1534 gave 0·3983 CO_2 and 0·0890 H_2O. $C = 70·81$; $H = 6·49$.

$C_{31}H_{32}N_4S_2$ requires $C = 70·84$; $H = 6·15$ per cent.

This compound dissolves sparingly in light petroleum or benzene, more readily in alcohol or ether, and easily in chloroform or glacial acetic acid. On warming with rectified spirit, hydrolysis takes place with liberation of formaldehyde, and, on heating with hydrochloric acid, formaldehyde and, finally, thiocarbimide are given off.

3-o-*Tolyl*-6-*methyl*-2-*thio*-1 : 2 : 3 : 4-*tetrahydroquinazoline*,



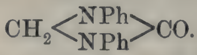
$$C_6H_4Me<\begin{matrix}NH-CS\\ \quad\ \ |\\ CH_2\cdot N\cdot C_6H_4Me\end{matrix}.$$

—In this experiment at the higher temperature (200°) no distillate collected. The residue, after cooling, consisted of a red, glassy mass; this was dissolved in hot alcohol, which, on standing, deposited crystals and finally an oil, which afterwards solidified. The crystals were redissolved in alcohol, from which glistening, colourless needles were obtained. The melting point is not sharp; the substance darkens above 230° and softens at 255°, complete fusion taking place at 262° (corr.):

0·1832 gave 0·4821 CO_2 and 0·1020 H_2O. $C = 71·74$; $H = 6·23$.
$C_{16}H_{16}N_2S$ requires $C = 71·60$; $H = 6·01$ per cent.

The compound is almost insoluble in light petroleum, not very soluble in alcohol or ether, more so in benzene, but dissolves easily in ethyl acetate, chloroform, or glacial acetic acid.

11. *Methyleneaniline and Phenylcarbimide.*



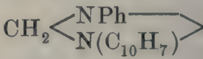
Methylenediphenylcarbamide, $\mathrm{CH_2}{<}\substack{\mathrm{NPh}\\ \mathrm{NPh}}{>}\mathrm{CO}$. — Methyleneaniline (1 mol.) was dried in a vacuum over phosphoric oxide dissolved in dry benzene, and phenylcarbimide (1 mol.) was added to the solution. The mixture, from which moisture was carefully excluded, was allowed to stand, when, in the course of a week, a crop of olourless crystals separated. After washing with dry benzene, the crystals melted at 197·5—198·5° (corr.):

0·2105 gave 23·2 c.c. N_2 (moist) at 18° and 766·5 mm. $N = 12·85$.
$C_{14}H_{12}ON_2$ requires $N = 12·50$ per cent.

Methylenediphenylcarbamide is insoluble in alcohol, very sparingly so in benzene, ether, or light petroleum, but dissolves easily in acids. On warming with acids, or even with water, hydrolysis takes place with formation of carbanilide and formaldehyde.

In the high temperature experiment in the case of the interaction of diphenylmethylenediamine and phenylcarbimide (section 1), evidence is given of the probable formation of this methylenecarbamide, although we were unable to isolate it. It was expected therefore that the compound would prove to be very unstable, as is now shown to be the case.

12. *Methyleneaniline and α-Naphthylcarbimide.*



Methylenephenyl-α-naphthylcarbamide, $\mathrm{CH_2}{<}\substack{\mathrm{NPh}\\ \mathrm{N(C_{10}H_7)}}{>}\mathrm{CO}$. — The reaction was brought about in exactly the same manner as in the last experiment. A small yield of colourless crystals separated from the ethereal solution on keeping. The melting point is not sharp; it depends on the rate of heating, and lies between 170° and 190°:

0·2168 gave 19·2 c.c. N_2 (moist) at 19° and 768 mm. $N = 10·29$.
$C_{18}H_{14}ON_2$ requires $N = 10·22$ per cent.

13. *Methyleneaniline and* p-*Tolylthiocarbimide.*

No reaction takes place at the ordinary temperature, and this appears to be the case generally with methyleneanilines and thiocarbimides.

It seems possible that at a higher temperature, owing to the para-position in the thiocarbimide being occupied, a quinazoline derivative might be formed. As already pointed out, this proved to be the case. The substances in equal molecular proportions were heated together at 200° for three hours. A dark red, viscid solid resulted, having an odour of thiocarbimide. This was dissolved in alcohol or benzene, from which crystals separated which were identified as 3-phenyl-6-methyl-2-thio-1 : 2 : 3 : 4-tetrahydroquinazoline. The yield of the base in this instance is inferior to that obtained by the reactions described in sections (4) and (8). It is associated with a red oil, from which it is difficult to separate.

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LXIV.—*Silicon Researches. Part XI. Silicotetrapyrrole.*

By J. EMERSON REYNOLDS.

MOST of the work recorded in former papers of this series dealt with the action of silicon halides on organic compounds which include the amino-group, such as the anilines, toluidines, and naphthylamines. In the course of the inquiry it has been shown for the first time that perfectly well-defined and often finely-crystallised substances can be obtained in which silicon is wholly combined with nitrogen. This new class of compounds, and their chief products of change, having now been sufficiently described, I propose to give an account of some similar work recently carried out with imides and nitriles.

The particular imide used was pyrrole, C_4H_5N, as its nitrogen forms part of a ring instead of merely serving for the attachment of a side-chain to a carbon ring; moreover, it was intended subsequently to apply a synthetic reaction of pyrrole to silicochloroform, as described in Part XII (this vol., p. 508), and a preliminary examination of the action of the base with silicon tetrachloride became necessary; the results obtained in this direction now follow.

When silicon tetrachloride and dry pyrrole are brought together, the two liquids do not mix, and no change occurs even on warming.

This indifference is in strong contrast with the violent action of aniline on the silicon halide under similar conditions. Addition of benzene, which mixes freely with both pyrrole and silicon chloride, does not lead to material interaction between the two substances; no sensible heat is evolved, although the mixture slowly assumes a brown colour, and a brown substance gradually deposits on the sides of the containing vessel.

The examination of this brown, amorphous substance ultimately led to the conclusion that it is a variable mixture of a condensed pyrrole, chiefly tripyrrole, with an additive compound of pyrrole and silicon tetrachloride. Several preparations were made and examined, but in no case did the percentage of silicon in the dry product exceed 3·61 per cent. Apart from the incidental production of the additive compound, it is evident that direct action of silicon tetrachloride on pyrrole is somewhat similar to that of hydrochloric acid and other acids in determining molecular condensation.

As direct attack was practically useless for the replacement of the imidic hydrogen in pyrrole, an indirect method was employed, which proved to be quite successful; this consisted in first forming potassium pyrrole, C_4H_4NK, and then acting on that substance with silicon tetrachloride.

Preparation of Potassium Pyrrole.

There is no material difficulty in the preparation of potassium pyrrole, but it is easy to destroy much expensive pyrrole in the process unless certain precautions are taken; hence a short description of the method which afforded me the best results may prove useful to others.

Twenty c.c. of dry pyrrole were diluted with about eight volumes of a petroleum which boiled at about 110°, that is, well above the melting point of potassium. Such a mixture was gently warmed, and metallic potassium was gradually added in small, *clean* pieces, the total weight required for the above volume of pyrrole being 11 grams. The addition of each piece of the metal caused brisk evolution of hydrogen, while potassium pyrrole separated out as a fine, nearly white precipitate. During the early stages of the preparation, the flask in which the operation took place required external cooling, but at the end, the temperature was raised so as to melt the potassium in order to secure complete action—hence the use of petroleum boiling about 110°. When all metallic particles had disappeared, the potassium pyrrole was rapidly collected (using a funnel plugged with asbestos) with as little exposure to air as possible; the precipitate was then well washed with light petroleum of low boiling point, and dried in a current of hydrogen. The slightly yellow-coloured powder so obtained must be carefully protected from moisture; otherwise it will quickly decompose, yielding potassium hydroxide and pyrrole.

Formation of Silicotetrapyrrole.

Silicon tetrachloride acts violently on potassium pyrrole, and much pyrrole is destroyed, but when the interaction is carried out as described below, it proceeds regularly in accordance with the equation:

$$SiCl_4 + 4C_4H_4NK = KCl + (C_4H_4N)_4Si.$$

Twenty-one grams of potassium pyrrole in very fine powder were placed in a flask fitted with a reflux condenser, and about 100 c.c. of light petroleum (b. p. 60—65°) were added. The flask was at first immersed in a freezing mixture of ice and salt, and when sufficiently cooled, a mixture of 8·5 grams of silicon tetrachloride, diluted with 50 c.c. of light petroleum, was gradually added, the contents of the flask being freely shaken. If the addition be very slowly effected, and the temperature be well kept down by cooling, comparatively little of the brown decomposition products are obtained. The potassium pyrrole should be in excess, and at the end of the operation a gram or so of the potassium compound was added, the mixture well shaken, and then allowed to stand overnight.

The separation of the silicotetrapyrrole formed from potassium chloride was effected in a Soxhlet extraction tube provided with a good layer of dry asbestos to act as a filter. The extractor was fitted in the usual way with flask and condenser, the former containing some light petroleum; when the process of extraction was started, the boiling light petroleum dissolved the silicopyrrole compound, leaving potassium chloride. Light petroleum was found to have the great advantage over benzene and other good solvents for the pyrrole compound in that it does not dissolve the brown-coloured by-products of the interaction.

The hot light petroleum solution in the flask deposits much of its silicopyrrole on cooling in the form of small, brilliant, and nearly colourless needles, which only require recrystallisation from fresh and boiling light petroleum for complete purification. With a sample so purified, the following analytical data were obtained:

0·0962 gave 0·23 CO_2 and 0·0508 H_2O. C = 65·2; H = 5·86.
0·1167 „ 18·35 c.c. N_2 (moist) at 18° and 770 mm. N = 19·06.
0·2197 „ 0·046 SiO_2. Si = 9·77.
0·2523 „ 0·0521 SiO_2. Si = 9·62.
$C_{16}H_{16}N_4Si$ requires C = 65·75; H = 5·48; N = 19·17; Si = 9·59 per cent.

Silicotetrapyrrole, $Si(NC_4H_4)_4$, when pure, crystallises from light petroleum in short, colourless prisms, but if the solution be very slowly cooled, they can be obtained from 2 to 3 cms. in length. The crystals melt at 173·4° (corr.); if the heating be continued, the liquid gradually darkens until it becomes almost black, while a portion volatilises and condenses in crystalline form on the sides of the tube in which the melting-point determination is carried out.

The substance is only slightly soluble in cold light petroleum, but is much more soluble in the boiling liquid. It is easily soluble without change in benzene, chloroform, or carbon disulphide. Anhydrous ether dissolves it without apparent decomposition; it is also soluble in absolute alcohol, but with ultimate decomposition.

The easy solubility of the compound in benzene, and the stability of the solution, rendered that solvent suitable for the determination of the molecular weight of the silicon compound by the boiling-point method. The data obtained, using a Beckmann's special thermometer, were as follows:

0·5304, in 13·187 benzene, gave Δt 0·37°; whence M.W. = 290.

$C_{16}H_{16}N_4$ Si requires M.W. = 292.

A similar determination of the molecular weight of silicotetraphenylamide gave 402, instead of 396 as required by the formula $Si(C_6H_5)_4$. There is therefore no doubt that both the pyrrole and the phenylamine silicon compounds exist as simple molecules in boiling benzene solution.

Silicotetrapyrrole is a comparatively stable substance in the absence of moisture and air. It does not give off pyrrole on heating until the temperature is so high that the material carbonises; and no such intermediate changes appear to take place as those observed and examined in the case of the compound $Si(NC_6H_5)_4$. This greater fixity is doubtless due to the fact that each nitrogen atom forms part of a pyrrole ring, and is externally combined only with silicon.

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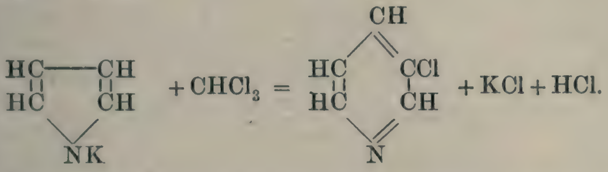
LXV.—*Silicon Researches. Part XII. The Action of Silicochloroform on Potassium Pyrrole.*

By J. EMERSON REYNOLDS.

THE facility with which the substance described in the preceding paper, $Si(NC_4H_4)_4$, can be obtained by interaction between silicon tetrachloride and potassium pyrrole, indicated the probability that silicochloroform, $SiHCl_3$, would afford at least the compound $SiH(NC_4H_4)_3$, and that it might be possible to form at the same time a compound including a carbon-silicon-nitrogen *ring*. The chief ground for the latter expectation is that ordinary chloroform and potassium pyrrole interact energetically and afford a small proportion of a chloro-substituted pyridine. This synthesis of pyridine from pyrrole may be represented as follows:



If silicochloroform, $SiHCl_3$, be analogous to chloroform, $CHCl_3$, in general relations as it is in composition, the former should be able to supply the SiH group required to form a silicopyridine ring from pyrrole. The experiments were made in the first instance with a view to applying this synthetic test, and the two substances were employed in equimolecular proportions.

Potassium pyrrole was placed in a flask, which was cooled to − 8° in a freezing mixture, and silicochloroform, also cooled, was allowed to drop on the solid pyrrole compound. Violent action took place with blackening and evident decomposition of pyrrole, the only recognisable product being a small proportion of silicotetrapyrrole.

Another experiment similarly conducted, but at the temperature of a mixture of solid carbon dioxide and alcohol, led to more definite results. In this case the silicochloroform used was previously diluted with twice its volume of a light petroleum which could be distilled without leaving any residue at 65°. In this case, also, vigorous action took place, even at the low temperature, but much less discoloration occurred. Every effort was made to secure complete interaction, and the mixture was allowed to stand for several days.

The contents of the flask when opened on the fourth day fumed much, indicating the presence of excess of silicochloroform. On distillation from a water-bath, about one-third of the silicochloroform was recovered unchanged along with all the light petroleum. A glycerol bath was then substituted for the water-bath and the temperature gradually raised to 135°, but only a few drops of liquid distilled, which included some free pyrrole. At 140° nothing further distilled, but on diminishing the pressure to 50 mm. several c.c. of a colourless, fuming distillate were quickly obtained. The dark residue did not give any further volatile matter on heating to a much higher temperature in a vacuum.

The fuming liquid so obtained, when redistilled, gave a portion boiling at 135°/50 mm., and this was found to be easily decomposed by water and to contain silicon, chlorine, and a pyrrole residue. This liquid gave Si = 17·2 and Cl = 44·4 per cent., approximately the ratio of Si : 2Cl, whilst $SiHCl_2 \cdot NC_4H_4$ requires Si = 16·87; Cl = 42·7 per cent.

The liquid is, no doubt, this monopyrrole derivative of silicochloroform, containing a little of the latter unchanged, and no trace of any substance of a pyridine nature could be obtained in the residue from which this liquid was distilled.

It was obvious from the result of the experiment just described that the use of a larger proportion of potassium pyrrole would probably lead to the formation of the substance $SiHCl(NC_4H_4)_2$, but it seemed inadvisable to use up valuable materials for this purpose, as it was more important to ascertain whether all the chlorine in silicochloroform could be replaced by pyrrole residues. The following experiment was therefore made.

Forty grams of potassium pyrrole were prepared as before, but instead of filtering off the product from the petroleum boiling below 110°, in which it was formed, the solid was allowed to remain diffused through the liquid in a very fine state of division. The flask containing this mixture was then connected with an apparatus supplying pure and dry hydrogen, so that the gas could be made to bubble through the turbid liquid. An arrangement was provided by means of which the gas current could be made to pass at will over 15 grams of silicochloroform contained in a bulb-tube, so that the vapour could be carried along and react with the potassium pyrrole. By careful management, this method worked well, and but little of the dark secondary products were formed. At the outset much heat was evolved, but it was considered preferable to keep this down by regulating the supply of gas and vapour rather than by external cooling. When all the silicochloroform had been passed into the mixture, the flask was sealed and its contents allowed to stand overnight. When the vessel was opened, there was no fuming, indicating that the silicochloroform was used up; nevertheless the mixture was heated for some time nearly to the boiling point of the petroleum and filtered while hot. The residue was repeatedly extracted with hot light petroleum (b. p. 70°) until nothing further was removed. That this extraction was complete there could be no doubt, as hot benzene failed to extract anything from the mass, which latter consisted almost wholly of the potassium chloride expected to result from the interaction.

The filtrates were mixed and formed a somewhat green-coloured liquid. This was distilled down to a small bulk, the distillate proving to be nearly quite free of any silicon compound. The residual liquid, which was now much more strongly coloured, gave, on cooling, groups of needle-like crystals. After separation of these, the liquid was further concentrated by distillation, and successive small crops of similar crystals were obtained.

This crystalline substance was purified by means of low-boiling light petroleum with as little loss as possible. The approximate weight obtained was 2·9 grams, and this resembled the compound described in the preceding paper, $Si(NC_4H_4)_4$, and melted at 173°:

0·245 gave 0·0513 SiO_2. Si = 976.

$C_{16}H_{16}N_4Si$ requires Si = 9·59 per cent.

There is therefore no doubt that it is silicotetrapyrrole, probably representing a small percentage of silicon tetrachloride in the silicochloroform.

The examination of the green residual liquid was then proceeded with. It was placed in a distilling flask, which latter could be connected at will with an air-pump. The liquid was heated gradually under the ordinary pressure until it reached 145°, at which nothing further distilled over. The distillate first obtained contained a little residue from the light petroleum, and some apparently unchanged pyrrole, but mere traces of any silicon compound.

The liquid was then slowly heated to 210°, and practically nothing distilled, but when that temperature was reached, there were signs of incipient decomposition; hence it was reduced to 200°, and the pressure gradually lowered to 25 mm. Even at this low pressure no further distillate could be obtained, and the temperature could not be pushed beyond 220° without decomposition. This liquid, which did not distil at 220°, even at low pressures, was of a very dark green colour. It did not deposit any crystalline or other matter on standing for more than a month, and appeared to be perfectly homogeneous. It was found to contain silicon and a pyrrole residue, and mere traces of chlorine; hence no chlorosilicopyridine could be present.

The following analytical data were afforded by this liquid:

0·5996 gave 0·1578 SiO_2. Si = 12·28.

0·2238 „ 34·6 c.c. N_2 (moist) at 15·1° and 766 mm. N = 18·11.

The ratio of Si : N is therefore 1 : 2·94.

$SiH(NC_4H_4)_3$ requires Si = 12·3; N = 18·49 per cent. Si : N = 1 : 3.

It is evident that in the course of the interaction which takes place, under the conditions stated above, between silicochloroform and potassium pyrrole, a large proportion of the former takes part only in the change represented by the equation:

$$SiHCl_3 + 3KNC_4H_4 = SiH(NC_4H_4)_3 + 3KCl.$$

The molecular weight of the liquid should be 227, and this was confirmed by a determination by the boiling-point method:

0·612 in 13·187 benzene gave Δt 0·56°. M.W. = 221.

This curious liquid did not exhibit any characters resembling those which a silicopyridine ring might be expected to possess; it is readily decomposed by water and alcohol, by acids and alkalis, although stable enough in light petroleum, benzene, carbon disulphide, or other indifferent solvents.

It is perfectly clear from the work described in this paper that silicochloroform does *not* act in a similar manner to ordinary chloroform with potassium pyrrole. The course of change taken by the former is such as we might expect a quasi-metallic chloride to follow; thus the analogy between silicon and carbon breaks down at this point, as at some others noted in the course of this study of the action of nitrogen compounds on silicon halides. Neither has silicon so far shown itself to be a "ring-" forming element like carbon. Silicon atoms have, in fact, but little tendency to unite *directly*—they seem to require the interposition of a multivalent element, such as oxygen, or a group, such as NH. The classical researches of Friedel, Ladenburg, and others have shown that in nearly all cases of silico-organic compounds the function of the single atom of silicon present in the molecule is quasi-nuclear. The same thing is noticeable in the recent and interesting extensions of the older work by Kipping and others; radicles may be varied indefinitely in silicon hydride, SiH_4, but the type remains.

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LXVI.—*Silicon Researches. Part XIII. Silicon Halides and Pyridine, Acetonitrile, etc.*

By J. Emerson Reynolds.

From the experience obtained with pyrrole, it was inferred that organic substances, including nitrogen wholly combined with carbon, would react feebly, if at all, with silicon halides. A series of experiments carried out in order to test this point confirmed this view in respect to pyridine, acetonitrile, propionitrile, and benzonitrile.

Pyridine reacts vigorously with silicon bromide and chloride, but with the former proceeds more regularly; hence the chief experiments were made with silicon tetrabromide.

Sixty-four grams (about 8 mols.) of freshly-distilled pyridine, diluted with 2 vols. of benzene, were gently warmed in a flask, and 35 grams (1 mol.) of pure silicon tetrabromide then gradually added. Much heat was evolved, and a white substance separated. When the addition was complete, the mixture was heated on a water-bath for an hour, in order to secure complete action.

The precipitate was collected, washed with pyridine, well drained by the aid of the pump, and dried over sulphuric acid for a week, in order to remove excess of pyridine. As pyridine hydrobromide is soluble in free pyridine and benzene, this product could only be a silicon compound. It is a white, amorphous powder, which fumes in moist air, and is resolved by water into pyridine hydrobromide, hydrobromic and silicic acids. The substance presented all the characters of an additive compound, and the analytical data confirmed that conclusion:

Found, Si = 5·82; Br = 64·2.

$SiBr_4,2C_5H_5N$ requires Si = 5·53; Br = 63·24 per cent.

The slight excess of silicon tetrabromide found is evidently due to some dissociation taking place on standing over sulphuric acid.

Silicon tetrachloride yields a similar additive compound,

$$SiCl_4,2C_5H_5N,$$

which was also obtained by Harden (Trans., 1887, **51**, 40), and need not be further noticed.

Acetonitrile.—8·5 c.c. of the nitrile, boiling at 81·6°, were added to 6·2 c.c. of undiluted silicon tetrabromide; these proportions represent 4 molecules of nitrile to one of the bromide. There was immediate action, and sufficient heat was evolved to require external cooling. A crystalline precipitate formed on standing. The mixture was sealed up in a tube, the contents warmed so as to dissolve the crystalline matter, and the tube then set aside for a considerable time. When next examined, an oily substance had separated from the liquid, and this gradually solidified to a crystalline mass.

This substance fumes in air, and it is easily decomposed by heat into silicon tetrabromide and the nitrile; it is therefore an additive compound. On analysis:

Found, Si = 6·6.

$SiBr_4,2(CH_3{\cdot}CN)$ requires Si = 6·51 per cent.

Propionitrile.—Eleven c.c. of the nitrile, boiling at 98°, were mixed with 6·2 c.c. of silicon tetrabromide. The liquids mixed freely, with very slight rise in temperature; no solid matter separated, even after standing in a sealed tube for some months, but droplets of an oil formed in the liquid when cooled. This oily substance, however carefully separated from the liquid in which it had formed, did not give concordant results on analysis; it seemed to be a mixture of a very feeble additive compound with an excess of silicon tetrabromide.

Benzonitrile, under similar conditions, did not afford any evidence of even feeble union with silicon tetrabromide or chloride.

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LXVII.—*The Ignition-Temperatures of Gases.*

By Harold Baily Dixon and Hubert Frank Coward.

The determination of the ignition-temperatures of inflammable gases has been attempted by numerous investigators in various ways; the results obtained are widely divergent, not only for separate series of observations, but to a smaller extent in each series.

The results of Sir H. Davy (*Phil. Trans.*, 1816, 7) are now interesting only from an historical point of view. He found that hydrogen and hydrogen sulphide inflamed when mixed with air at "the lowest visible heat of iron and charcoal." Ethylene and carbon monoxide were fired by both charcoal and iron heated to redness. Methane was not inflamed by an iron rod at "the highest degree of red heat, and the common degree of white heat," but an iron rod "in brilliant combustion" succeeded.

Bunsen (*Gasometrische Methoden*, 1st edition, 1857, 2nd edition, 1877) determined the limiting dilution of electrolytic gas with hydrogen, oxygen, and carbon dioxide beyond which the mixture was no longer inflammable. The temperature of the flame which travelled through the mixtures that were only just inflammable was calculated. This he regarded with some hesitation in the first edition of the *Gasometrische Methoden* as the ignition-temperature of hydrogen. In the second edition he quoted only the corrected number for the oxygen dilution experiments as the ignition-temperature, namely, 743·6°. Bunsen's method is open to two main objections, first, the fact that electrolytic gas alone does not ignite with an ordinary spark below 70 mm. pressure (Meyer and Seubert, Trans., 1884, **45**, 587; H. B. Dixon, *Phil. Trans.*, 1884, **175**, part 2, 634), and, secondly, the results obtained with different diluents are widely discordant, namely, 2116°, 1760°, and 857° are given for the ignition points of hydrogen when carbon dioxide, hydrogen, and oxygen respectively are used as diluents.

More recent investigations may be classed into three main groups according to the experimental conditions:

I. A bulb containing the mixed gases was plunged into a bath at constant temperature;

II. A stream of the mixed gases was passed through a tube in a bath which was being gradually heated up;

III. The adiabatic compression, just sufficient to cause ignition, was used to calculate the temperature of the mixture at the ignition point.

The results obtained by these methods for hydrogen and oxygen are collected in the following table:

TABLE I.

Method.	Observers.	Ignition-temperatures.
I.	V. Meyer, Krause, Askenasy[1] ...	518—606°
	Emich[2]	589 571—608 (with excess of oxygen). 575—607 (with excess of hydrogen).
II.	Mallard and Le Chatelier[3]	550
	Bodenstein[4]	653—710
	Mitscherlich[5]	674
	V. Meyer and Freyer[6]	700
	Gautier and Helier[7]	840
	Helier[8]	845
III.	Falk[9]	540 ($2H_2+O_2$) 514 (H_2+O_2) 530 (H_2+2O_2)

It is to be noted that when the gases were heated in sealed bulbs the pressure at the ignition point was roughly three times the initial pressure; and when the gases were fired by adiabatic compression the pressure at the ignition point was roughly thirty-nine times the initial pressure.

The observations recorded for gases other than hydrogen are very few.

Mallard and Le Chatelier found, by passing different mixtures of carbon monoxide and oxygen or air through a heated tube, an ignition-temperature of 630—680°. Dilution with carbon dioxide raised the ignition-temperature to 695—725°. These investigators also gave 600—660° as the ignition-temperature of methane.

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[1] *Annalen*, 1891, **264**, 85 ; 1892, **269**, 49. *Ber.*, 1892, **25**, 622 ; 1893, **26**, 429, 2421. *Zeitsch. physikal. Chem.*, 1893, **11**, 28.

[2] *Monatsh.*, 1900, **21**, 1061.

[3] *Compt. rend.*, 1880, **91**, 825.

[4] *Zeitsch. physikal. Chem.*, 1899, **29**, 665.

[5] *Ber.*, 1893, **26**, 163.

[6] *Ber.*, 1892, **25**, 622.

[7] *Compt. rend.*, 1896, **122**, 566.

[8] *Ann. Chim. Phys.*, 1897, [vii], **10**, 521.

[9] *J. Amer. Chem. Soc.*, 1906, **28**, 1517 ; 1907, **29**, 1536.

V. Meyer and Freyer (*Zeitsch. physikal. Chem.*, 1893, **11**, 28) obtained the following limiting values for ignition-temperatures:

TABLE II.

Mixture.	Ignition-temperature of Free current of gas.	Ignition-temperature of Gas in closed bulb.
Methane and oxygen	650°—730°	606°—650°
Ethane and oxygen	606 —650	530 —606
Ethylene and oxygen	606 —650	530 —606
Carbon monoxide and oxygen	650 —730	650 —730
Hydrogen sulphide and oxygen	315 —320	250 —270
Hydrogen and chlorine	430 —440	240 —270

V. Meyer and Münch (*Ber.*, 1893, **26**, 2421) employed rather later the following improved method. The explosive mixture was passed through a capillary tube to the bottom of a small glass vessel inserted in the bulb of an air thermometer. When the mixture inflamed, the air of the thermometer bulb was displaced by hydrogen chloride and measured over water. This gave the temperature of ignition.

The following are the results obtained:

TABLE III.

Mixture.	Ignition-temperature.	
Hydrogen and oxygen	620—680°	
Carbon monoxide and oxygen	Combined quietly.	
Hydrogen sulphide and oxygen		
Methane and oxygen	656—678°	
Ethane and oxygen	605—622	Three experiments each.
Ethylene and oxygen	577—590	
Acetylene and oxygen	509—515	
Propane and oxygen	545—548	
Propylene and oxygen	497—511	
*iso*Butane and oxygen	545—550	
*iso*Butylene and oxygen	537—548	
Coal gas and oxygen	647—649	

The chief source of disagreement in the preceding results is probably to be found in the influence of surface action. Thus the results of Helier and of Gautier and Helier were obtained by passing electrolytic gas through a tube packed with pieces of glazed porcelain, an experimental method which increased the slow surface combination enormously and resulted in an ignition-temperature nearly 300° higher than that found by Mallard and Le Chatelier.

In the method of adiabatic compression used by Falk at Professor Nernst's suggestion, fourteen experiments with electrolytic gas gave numbers from 518° to 569°, with a mean of 540°. In these experiments ignition occurred under some 35 to 70 atmospheres pressure, a very different condition from that of previous experiments. Our experiments show that the ignition point of electrolytic gas falls with increase of pressure.

The present set of experiments is based on the definition of ignition-temperature as that temperature to which the gases must be separately heated, so that when brought into contact they will inflame immediately.

The method used by us was designed by Professor Dixon in 1903, the first apparatus being constructed by Mr. G. W. A. Foster, B.Sc.*

An atmosphere of oxygen or air passed slowly upwards through a large porcelain tube, the temperature of which could be gradually raised by means of an electric current traversing a close spiral of platinum wire wound round the outside of the tube. The inflammable gas was led up a narrow tube fixed in the axis of the larger porcelain one, so that the gases were heated to the highest temperature of the tube before they came into contact. The temperature of the gas was recorded by a thermo-junction inserted just below the orifice of the narrow inner tube. The flowing current of gas ensured the supply of fresh, hot gas, and the removal of products of slow combustion. This arrangement, described in detail below, also enabled the effect of surface influence to be minimised. Working with different tubes, we found that a constant ignition point was obtained when both the diameter of the outer tube and the rate of the stream of combustible gas issuing through the orifice surpassed a certain minimum value. With an outer tube of 45 mm. diameter and an orifice of 1 mm. diameter, the stream of hydrogen had to be passed at a rate exceeding 9 c.c. per minute to give a constant ignition-temperature. The same constant was reached in a wider tube with a faster flow of hydrogen.

That the ignition-temperature of a jet of hydrogen should fall with an increase in the diameter of the outer tube containing the oxygen, and for a given diameter of outer tube should fall with an increase in the speed of the jet, seemed explicable on two hypotheses:

(1) It might be supposed that a stream of hydrogen escaping very slowly into an atmosphere of oxygen would diffuse more rapidly into the oxygen than a quicker stream rising in an unbroken cylinder for some distance above the orifice. In the diffused gases quiet combustion might begin, and the steam so formed, diluting the mixture, might raise the temperature of ignition of the residue. The difficulties of such an explanation are twofold. The quiet combustion would heat the mixture and tend to lower rather than raise the apparent ignition point; and, secondly, when the hydrogen

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* This apparatus, with which the ignition-temperature of hydrogen in oxygen was found to be from 610° to 616°, was exhibited at the Royal Society in 1904.

was diluted with nitrogen, or with steam, or with oxygen (which would form steam just before the gas issued from the orifice), no raising of the ignition point was observed. Similarly, the substitution of air for oxygen in the outer tube made no difference in the ignition point. The "dilution" hypothesis is therefore untenable.

(2) Since the gases inflame at a lower temperature when they are removed further from the hot surfaces of the outer tube and from the hot mouth of the inner tube, these hot surfaces must retard the chemical action. Now it has been shown by the photographic analysis of explosion flames that, when an explosive mixture is ignited in a tube by a small spark, the gases continue to burn with a nearly constant intensity for a comparatively long period, so long as they are undisturbed by compression waves. When a compression wave strikes such a burning mixture the rapidity of combustion is greatly increased. In this way it can be shown that in a freshly ignited flame of electrolytic gas the number of "chemically fruitful" collisions between hydrogen and oxygen molecules is only a small fraction of the total collisions.

On the other hand, from Maxwell's law of the distribution of speeds among gaseous molecules we find that about 3 per cent. of the molecules have a speed twice as great as the "most probable speed." In a gaseous mixture the mean temperature of which is approaching the ignition point, chemical action would begin among these more rapidly moving molecules. Now the presence of a solid body at the mean temperature of the gas would tend to equalise the speed of the molecules coming into contact with it, accelerating the slow, but checking the rapidly moving. The hot walls would therefore hinder the initial chemical combustion, due to collisions "out in the open," and *pro tanto* raise the ignition point. But the solid wall would also take up the heat from such steam molecules as were formed on or near its surface, and prevent them communicating their energy to the unburnt gases round them.

It may be assumed that the width of the outer tube chiefly affects the movements of the oxygen molecules, while the rapidity of the stream of hydrogen affects the movements both of the hydrogen and oxygen molecules as they diffuse into each other round the orifice of the inner tube. This hypothesis seems to account for the observations, and also to explain why, *ceteris paribus*, a larger orifice, by offering a less surface to the mixed gases, gives a lower ignition point when the jet is issuing comparatively slowly.

The results we have obtained for the ignition-temperatures of gases at normal pressure may be summarised thus:

TABLE IV.

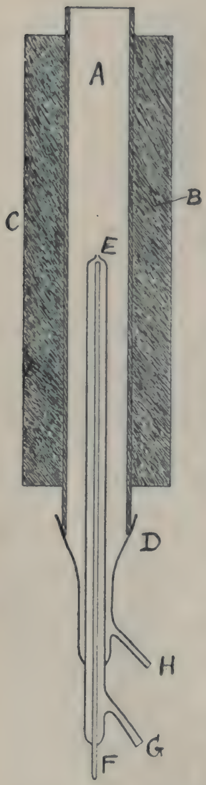
	Ignition-temperature			
	In oxygen.		In air.	
	Between	Mean.	Between	Mean.
Hydrogen	580—590°	585°	580—590°	585°
Carbon monoxide (moist) ...	637—658	650	644—658	651
Cyanogen	803—818	811	850—862	856
Ethylene	500—519	510	542—547	543
Acetylene	416—440	428	406—440	429
Hydrogen sulphide	220—235	227	346—379	364
Methane	556—700	—	650—750	—
Ethane	520—630	—	520—630	—
Propane	490—570	—	—	—
Ammonia	700—860	—	—	—

EXPERIMENTAL.

The ignition-temperature of a jet of combustible gas flowing into an atmosphere of oxygen or air has been determined in various forms of apparatus, of which that sketched in Fig. 1 includes the most important features. It consisted of a wide porcelain tube (*A*), 45 mm. internal diameter, wrapped round with a sheet of platinum foil covered with an insulating coating of asbestos paper, round which was bound a platinum wire, 0·009 inch in diameter, four turns per cm. This wire served as a resistance for the current of two to four amperes used for heating the tube. Loss of heat by radiation was diminished by a thick covering of asbestos packing or kieselguhr (*B*), held together by a hollow cylinder of asbestos board (*C*). This in turn was wrapped in aluminium foil in order to reduce further the loss of heat by radiation. The lower end of the broad porcelain tube was ground to fit closely into the wide end of the funnel (*D*), the joint being made air-tight by mercury. Into the narrow end of the funnel was fused a long tube terminating in an orifice (*E*) in the centre of the porcelain tube. Coaxial with this tube was a narrower one (*F*) reaching to within two millimetres of the orifice and closed at the upper end. This was used to contain a thermo-junction, which therefore registered the temperature of a gas as it was just about to pass through the orifice. The combustible gas was admitted by the side-tube (*G*), and a similar side-tube (*H*) supplied an entrance for the air or oxygen to surround the jet.

Several modifications of this apparatus have been used. The diameter of the orifice has been varied between about 0·6 mm. and 2·1 mm. The material of the nozzle has been varied by using tubes of silica, Jena combustion glass, boro-silicate, and soft soda glass ground into the glass base just above the entry tube (*G*). For high temperature work the thermo-junction cover and the nozzle were both of fused quartz ground into the glass base. For many of the series of experiments recorded, similar apparatus with porcelain tubes of half and double the diameter of the one figured were used.

FIG. 1.



For a few experiments with hydrogen, details of which are given below, the thermo-junction in a suitable cover was inserted from the top end of the apparatus, and was suspended above the orifice in order that it might indicate the temperature of the mixing gases rather than that of the gases just before admixture. The results obtained were just the same as those with the ordinary form of apparatus.

Further to test this, two thermo-junctions were arranged in opposition, and connected up with the galvanometer, so that any movement of the beam of light from the galvanometer would indicate a difference of temperature between the thermo-junctions. One of them was placed as usual inside the nozzle, the other in a thin Jena glass cover at various heights above the orifice. There was never more than two degrees difference until ignition took place, although the position of the upper thermo-junction was changed from 1 mm. to 40 mm. from the orifice.

The Thermo-junction.—A fused junction of platinum and platinum-iridium alloy was used, connected (in a case kept at a constant measured temperature) with an Ayrton-Mather dead-beat galvanometer. The readings were observed to about 0·7°. For calibration the following melting points were used, for which we wish to thank Dr. Harker, of the National Physical Laboratory, and Mr. A. F. Edwards, of the Manchester University:

Lead	327°	
Lithium chloride	605	±0·5°
Aluminium	652·5	±1
Potassium chloride..........................	775	
,, carbonate	835	±3

Method of Experiment.—The furnace was gradually heated at various rates, usually about 5° per minute, from some 50° below the expected temperature of ignition. During this time the combustible gas and the atmosphere required for its combustion were being supplied through the side-tubes (*G*) and (*H*). The furnace was so wound that its maximum temperature was at the level of the thermo-junction; above this point the temperature was uniform (within 2°) for a distance of 50 mm.

Thus the reacting gases were brought into contact at the temperature recorded by the thermo-junction; and no reaction had occurred to either gas during the progress of the heating; for not only did the two gases remain separate until they were fully heated, but in each case the gas passed through the hot tube much too quickly for any appreciable thermal decomposition to have taken place* before combustion.

The manner in which a gas passes through a jet inside a tube may be observed by passing a cloud of smoke in suspension up the inner tube: the gas rises in the form of a thin cylinder, of length up to four or five inches, but varying considerably with the rate of flow of the gas.

By looking down the tube, ignition was observed to occur just above the orifice, a small ball of gas igniting with a sharp crack, and leaving a smaller flame burning quietly at the orifice.

Preparation of the Gases.—These were obtained in the usual ways, and after chemical purification were, whenever possible, subjected to liquefaction by means of liquid air, and subsequent fractional distillation. Hydrogen was obtained by the electrolysis of recrystallised baryta, with elimination of oxygen. When possible, the gases were roughly dried by calcium chloride or sulphuric acid.

Measurement of the Rate of Flow of the Gases.—The rate of flow of hydrogen was obtained by observing the amperage of the current used for electrolysis of the baryta; for one ampere produces almost exactly 7 c.c. per minute, measured at 0° and 760 mm. For the other gases not soluble to a great extent in water or sulphuric acid, the number of bubbles passing through a worm or similar apparatus per minute gave, after calibration, the rate of flow with fair accuracy.

For ammonia and cyanogen, which could not be treated thus, mercury was allowed to drop at a measured rate into the reservoir of a gas holder, the outlet tube for the gas being kept open all the time. Backward diffusion of air into the gas was prevented by the use of a capillary tube between the gas holder and the ignition-temperature apparatus.

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* For the action of heat on methane, ethane, ethylene, and acetylene, see Bone and Coward, Trans., 1908, **93**, 1197.

Ignition-temperature of Hydrogen in Oxygen.

The ignition-temperature of hydrogen has been observed under variation of the following conditions of experiment:

(1) The rate of flow of hydrogen through the orifice.

(2) The rate of flow of oxygen surrounding the jet.

(3) The diameter of the orifice through which the hydrogen flowed.

(4) The composition and physical nature of the materials of the nozzle.

(5) The composition, physical nature, and distance from the jet of the walls of the furnace.

(6) The rate of rise of temperature of the furnace.

(7) The position of the thermo-junction: (*a*) inside the hydrogen nozzle; (*b*) just above the nozzle, where the hydrogen and oxygen are combining.

(8) The variation of pressure of the gases.

The Ignition-temperature of Hydrogen Flowing at Rates up to 19 c.c. per minute.—The narrowest furnace was employed. Its tube was of glazed Berlin porcelain, internal diameter 20 mm. The nozzle was of quartz, the orifice in it being 0·99 mm. internal diameter. The rate of flow of oxygen was maintained at approximately 50 c.c. per minute.

The following results were obtained:

TABLE V.

Rate of flow of hydrogen, c.c. per min.	Ignition-temperature.	Nature of ignition.
2·4	792°	Quiet
3·1	750	,,
3·5	730	,,
3·8	712	,,
4·2	693	,,
5·2	662	,,
7·0	608	Gentle explosion
14·0	602	Moderate ,,
14·0	600·5	,, ,,
17·5	599	Loud ,,
19·0	599	,, ,,

These results are plotted in Fig. 2, which shows that under these conditions the ignition-temperature is nearly constant for rates of flow from 7 c.c. per minute to 19 c.c. per minute. In this curve the abscissæ represent rates of flow of hydrogen, ordinates the corresponding temperatures of ignition. Its peculiarity is its sudden upward turn, showing the great rise in ignition-temperature which occurs when the rate of flow of hydrogen is decreased below 7 c.c. per minute.

The Ignition-temperature of Hydrogen under Different Rates of Supply of Oxygen.—The narrowest furnace was again employed, but the orifice was somewhat wider, being 1·24 mm. in diameter. The following results were obtained:

TABLE VI.

Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
3·4	40	751°
3·5	53	760
4·3	40	735
4·5	47	723
4·6	36	725
4·9	25	739
4·9	93	719
5·5	23	714
5·7	43	618
5·7	50	614
6·0	29	608
6·0	67	671
6·0	100	662
6·8	60	606
7·0	20	608°
7·0	50	608
7·0	53	616
7·0	60	600
7·0	87	604
14·0	25	602
14·0	53	608
14·0	60	602
14·4	87	601
14·7	43	604
19·6	53	609
21·0	53	607
21·0	60	606
22·0	50	609

For convenience of graphic representation (see Fig. 3), these results are brought into four groups, in each of which the rate of flow of oxygen is roughly constant, as follows:

(*A*).	Oxygen rate	20 c.c. per minute.........	Curve 2
(*B*).	,, ...	40 ,, ,, ...	,, 3
(*C*).	,, ...	55 ,, ,, ...	,, 4
(*D*).	,, ...	90 ,, ,, ...	Stars

As in Fig. 2, the abscissæ represent rates of flow of hydrogen, the ordinates ignition-temperatures.

The sudden change in direction of the curve when the rate of flow of hydrogen is about 7 c.c. per minute is repeated in all four curves.

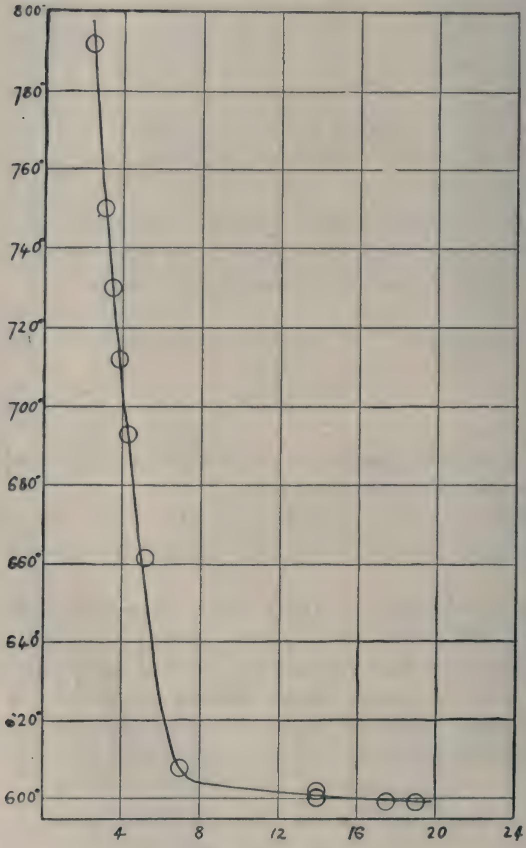
Variation of the Size of the Orifice.—The experiments already quoted were performed with quartz nozzles the orifices of which were 0·99 and 1·24 mm. diameter. Several series of experiments were done with a quartz nozzle having an orifice of 2·12 mm. internal diameter, with the results tabulated below. In this series, also, the narrowest porcelain tube was employed.

TABLE VII.

Diameter of orifice, 2·12 mm.

Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
2·8	37	No ignition below 760°
4·2	37	605°
5·6	38	606
6·8	44	605
7·0	60	604
7·0	40	604
9·1	42	606
17·4	50	605

FIG. 2.

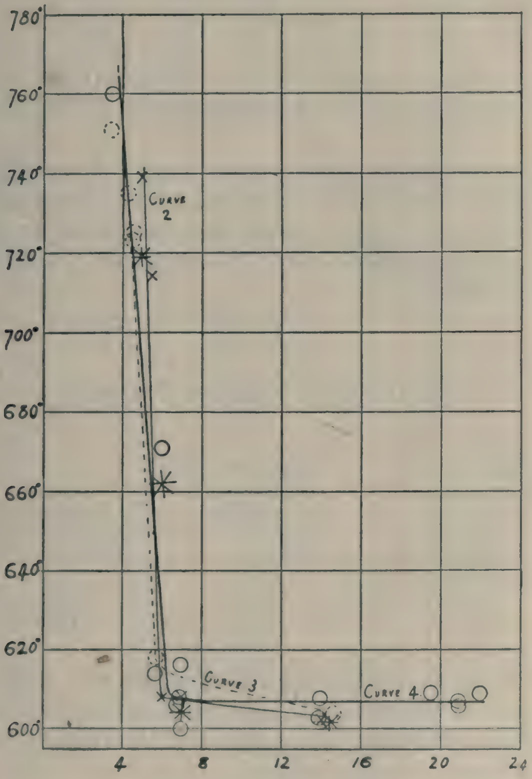


C.c. of hydrogen per minute.

With an orifice of more than double the diameter and nearly five times the area of the first one used, the same constant ignition-temperature is obtained. There is one peculiarity of this series, namely, that when the rate of flow of hydrogen fell below 7 c.c. per minute ignition still occurred between 600° and 610°, whereas when the narrower orifices were used the ignition-temperature rose rapidly with decreasing rates of flow.

The suggestion that this quick rise in ignition-temperature with decrease in rate of flow of hydrogen was due to the influence of the surface of the nozzle on the mixture of the hydrogen and oxygen is confirmed by this experiment. A larger orifice means that a less fraction of the gas passing through it comes into contact with it in inverse ratio to the diameter of the orifice.

Fig. 3.



C.c. of hydrogen per minute.

Variation of the Composition and Physical Nature of the Nozzle.—Several nozzles of different materials were ground into the glass base of the apparatus; and in order to accentuate any specific effect of the material, the thermo-junction was placed in a tube of the same material suspended just above the nozzle. The orifices were approximately 1 mm. in diameter.

TABLE VIII.

Outer porcelain tube, 20 *mm. diameter.*

Material of jet.	Ignition-temperatures.
Quartz	612°, 610°.
Boro-silicate glass	608°, 612°, 612°, 610°, 600°, 601°, 602°, 599°.
Soda glass	606°, 607°.

Since the three series of numbers are practically the same, it seems as if ignition took place independently of the nature of the nozzle.

A new quartz tube was drawn out and cut. Normally the nozzle would have been used in this condition with a smooth surface, but in this case it was rubbed down and roughened by being held against a revolving grindstone. The result of a series of experiments was as follows:

TABLE IX.

Diameter of orifice, 1·34 *mm. Diameter of outer porcelain tube*, 20 *mm.*

Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
5·3	32	No ignition below 740°
5·5	40	,, ,,
5·5	47	,, ,,
6·9	39	611°
17·9	47	607

In the first three experiments recorded the cold watch-glass over the upper end of the porcelain tube became covered with globules of moisture soon after the temperature of the furnace had reached 600°, but a flame did not appear.

Variation of the Composition, Physical Nature, and Distance from the Nozzle, of the Walls of the Furnace.—A new apparatus constructed with a porcelain tube of slightly greater diameter, 22 mm. instead of 20, gave the following results:

TABLE X.

Diameter of orifice, 1·19 *mm.*

Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
4·3	18	No ignition below 850°
4·3	31	
4·3	56	
5·6	45	598°
5·7	27	598
5·7	27	598
7·7	64	603
7·8	64	602
8·0	27	591
8·0	27	599
11·6	90	595°
15·8	90	594
15·8	110	595
16·6	110	594
17·1	31	594
17·5	31	598
17·8	99	597
17·8	99	597
17·8	99	597

The ignition-temperature is still independent of the rates of flow of hydrogen and of oxygen, but lies some 10° lower than the numbers found with the slightly narrower apparatus.

An apparatus was next constructed in which the porcelain tube had a diameter of 45 mm., slightly more than twice the diameter of the tubes used previously (see Fig. 1).

A glass nozzle with orifice of 1 mm. diameter gave the following results for two different rates of flow of oxygen:

TABLE XI.

Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
5·2	38	No ignition below 630°
9·1	38	588°
10·1	38	587
10·5	38	584
13·6	38	587
13·6	38	587
8·1	86	No ignition below 630°, but water condensed.
8·1	86	
12·4	86	584°
14·7	86	584
16·1	86	586

It is evident that the widening of the tube has affected the ignition-temperature appreciably, and that 584—588° represents the constant obtained as ignition-temperature with a tube of 45 mm. diameter. To determine whether this is independent of the nature of the nozzle and its diameter, as was the case with the narrower tube, the following series of experiments was performed:

Table XII.

Nozzle.		Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
Material.	Diameter.			
Glass	2 mm.	11·9	60	582°
Quartz	1·3 mm.	12·0	50	589
,, ...	1·3 ,,	11·9	67	590
,, ...	1·3 ,,	12·1	22	589

If we set the ignition-temperature at 580—590°, there is no variation within those limits due to the change in the above conditions of the experiment.

It was necessary, however, to see whether the ignition-temperature was further lowered by the enlargement of the tube. For this purpose a tube of 90 mm. diameter, that is, twice the diameter of the tube used previously, was bound with nickel wire, and so made into an electric resistance furnace. It was fitted at the bottom with a fireclay plug, bored for the admission of a nozzle containing a thermo-junction cover, and supply tube for oxygen. A glass nozzle with an orifice of 1·5 mm. diameter was used.

Table XIII.

Rate of flow of hydrogen, c.c. per min.	Ignition-temperature.	Rate of flow of hydrogen, c.c. per min.	Ignition-temperature.
17·5	No ignition	92	593°
25	659°	92	590
28	655	92	592
35	633	115	592
56	607	140	593
65	603	150	594
70	599		

Oxygen was supplied at the rate of about 150 c.c. per minute; a small amount of air may have mixed with it by diffusion.

Ignition seemed to occur in each case just above the orifice, and was never at all noisy. The rate of the hydrogen stream had to be much faster in this wider tube before a constant ignition-point was reached.

The ignition-temperatures thus obtained are just over 590°. The number 580—590° obtained in the tube of diameter 45 mm. is the limit to which the ignition-temperature may be reduced by widening the tube.

To determine whether any swirling of the gas in the larger tubes caused the decrease in ignition-temperature, a ring of loose asbestos, forming a filter, was put into the tube just below the jet, and the following series of results obtained in the 45 mm. tube:

Table XIV.

Depth of plug from jet.	Orifice diameter, in mm.	Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
28 mm.	0·53	14	53	589°
28 ,,	0·53	14	60	587
28 ,,	0·53	14	170	582
14 ,,	0·53	14	60	595
14 ,,	0·53	14	71	589
14 ,,	1·04	14	44	584
14 ,,	1·04	14	45	587
14 ,,	1·04	14	118	585

These results are practically the same as the previous ones obtained in this tube.

The apparatus with 45 mm. tube was also used for a series of experiments in which tubes of various materials and various diameters were inserted co-axially with the nozzle. This was the same in effect as constructing a series of furnaces from different materials and of different dimensions. For all the experiments, the nozzle was of glass, the orifice of 0·53 mm. diameter, the rate of flow of hydrogen 14 c.c. per minute, of oxygen 50 c.c. per minute.

Table XV.

Internal diameter of inserted tube, in mm.	Material of inserted tube.		
	Jena glass.	Glazed porcelain.	Rough porcelain.
13	613°	—	—
	610	—	—
15	601	—	—
	605	—	617°
	603	—	—
16	—	614°	—
18	597	—	—
	597	—	—
22	—	597	—
	—	596	—
	—	601	—
28	584	—	—
	584	—	—
45	—	591	—
	—	589	—
	—	592	—

The results indicate that with the narrower tubes glass gives a somewhat lower ignition-temperature than porcelain; but with wider tubes this difference is smaller and within the limit of 10°, which seems to be the experimental error of the method.

An interesting point in the above experiments was that ignition occurred in the narrower tubes with a sharp crack, in the wider tubes with much less noise.

Variation of the Rate of Rise of Temperature of the Furnace.—The last three experiments of table X are results obtained thus: First, with a normal rate of rise of temperature; second, with a slower rate; third, with a rise of about one degree per minute. Other similar tests gave results which never differed more than three degrees.

Variation of the Position of the Thermo-junction.—In the series of experiments previously described, the temperature of ignition was obtained by observing the temperature of the hydrogen 2 mm. below the orifice. Some experiments performed with the thermo-junction suspended in a quartz cover just above the orifice, that is, in the mixing gases, gave these results in the narrowest tube:

599°, 599°, 601°, 601°, 604°, 602°.

These results are to be compared with the last four experiments of table V.

Variation of the Pressure of the Gases.—The ordinary variations of barometric pressure had no appreciable effect on the ignition-temperature, for example:

TABLE XVI.

Barometer.	Ignition-temperature.
765·5 mm.	604°
760 ,,	602
752 ,,	600°, 604°

A new apparatus was constructed to determine ignition-temperatures under low and high pressures. It was essentially the same as the forms previously described, but instead of a porcelain tube forming the inner wall of the furnace, a glass tube was employed in order that the ends might be closed. The entrance tubes for hydrogen and oxygen were attached by special joints of hard and soft glass to the drying apparatus, the bubbler for measuring the rates of flow of the gases, and finally the gasholders. The joints were all of fused glass. For experiments under pressures of more than one atmosphere, the hydrogen was stored in a mercury gasholder and the pressure applied by means of a column of mercury; the oxygen was obtained from an iron cylinder. The exit tube of the furnace was attached to a conical brass tap for regulating the rate of escape of the gases. For experiments under reduced pressure the tap was connected with a water-pump.

The internal diameter of the glass tube was 25 mm., of the orifice 1·5 to 2·0 mm.

This apparatus survived experiments under pressures from 425 to 1520 mm., but burst near the top when heated under 1900 mm.

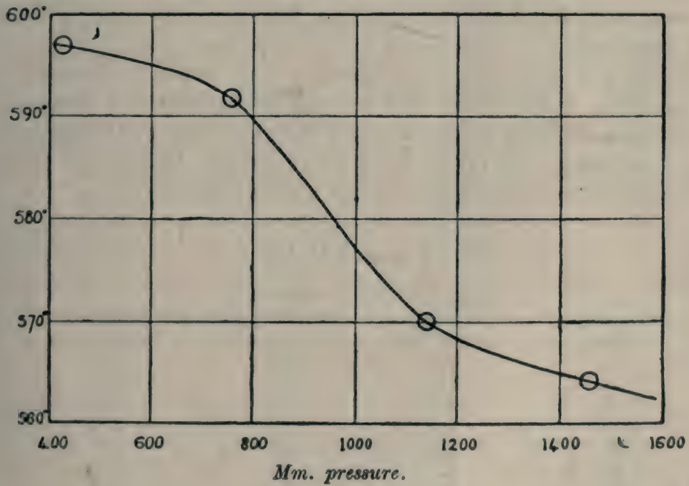
TABLE XVII.

Pressure, in mm.	Rate of flow of hydrogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	Means.
428	21	60	597°	597°
425	34	60	597	
425	34	60	597·5	
523	21	64	598	
573	21	64	598	
760	23	58	593	592
760	19	58	592	
760	21	58	591	
760	21	58	592	
880	21	58	586	
960	21	58	580	
1030	21	100	577	
1120	21	58	573	570
1140	21	58	571	
1140	21	58	567	
1450	21	58	566	564
1460	21	58	562	
1460	21	58	564	

The four numbers in the last column, means of several closely agreeing results, are represented in Fig. 4.

Whilst there is only a small elevation of ignition-temperature when the pressure is reduced to almost half an atmosphere, there is a fairly large lowering when the pressure is increased above one atmosphere. But the lowering of ignition-temperature on increasing the concentration of the gas, while fairly rapid up to one and a-half atmospheres, is much slower afterwards. If the

FIG. 4.



pressure were increased considerably more, it seems possible from the curve that the ignition-temperature might become constant between 550° and 560°.

Ignition Temperature of Hydrogen Mixed with Various Diluents.

These experiments were performed in order to determine whether the apparatus used would show any alteration in the ignition-temperature of hydrogen if that gas were previously diluted with substances such as might be present in the gases mixing just above the orifice, for example, oxygen, steam, nitrogen.

The medium-size apparatus was used, with an extra side-tube to enable a thermometer to be introduced to record the temperature of the water placed in the inner, hydrogen, tube for those experiments in which the effect of steam was tried.

Influence of 4 per cent. of Oxygen in the Hydrogen.—Four experiments were performed with rates of flow of inflammable gas and oxygen of 15 and 65 c.c. per minute respectively. The first and last experiments were performed with pure hydrogen, the second and third with hydrogen containing 4 per cent. of oxygen. The ignition-temperatures obtained were: (1) 590°, (2) 593°, (3) 590°, (4) 593°. When a small coil of platinum wire was put into the inner tube just below the orifice, the numbers 589°, 587°, 585° were obtained with the 4 per cent. oxygen mixture, 590° and 585° with pure hydrogen.

Influence of Steam in the Hydrogen.—A few c.c. of water were put into the inner tube, and heated electrically by means of a coil of platinum wire wrapped round the glass base of the apparatus. Its temperature was taken by a thermometer introduced through a side-tube. The following results were obtained:

TABLE XVIII.

Percentage of steam.	Rate of flow of mixture, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
0	14	70	587°
0	15	68	584
0	15	68	584
0	15	69	583
18	16·5	68	589
20	17	70	581
45	20·5	70	584
43	20	70	581
43	14·5	70	587

Influence of Nitrogen in the Hydrogen.—A mixture of equal volumes of hydrogen and nitrogen were passed through the orifice at a rate of 40 c.c. per minute, so that hydrogen itself was passing at 20 c.c. per minute. The ignition was somewhat quieter than when pure hydrogen was employed, and the flame somewhat larger.

Table XIX.

Rate of flow of hydrogen and nitrogen mixture, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.
40	71	580°
40	110	583
40	110	581

These numbers agree with the corresponding temperatures for pure hydrogen.

The Ignition-temperature of Hydrogen in Air.

The air used for the following experiments was previously purified by passage through aqueous potassium hydroxide and concentrated sulphuric acid.

Experiments in the Narrowest Apparatus.—The following series of results was obtained with the porcelain tube of 20 mm. diameter:

Table XX.

Diameter of orifice, mm.	Rate of flow of hydrogen, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.
1·34	7·1	44	612°
1·34	17·9	67	607
2·12	3·6	40	610
2·12	4·8	42	609
2·12	7·0	36	609
2·12	10·1	32	609
2·12	17·9	56	607

Experiments in the Wider Apparatus.—The following series of results was obtained with the porcelain tube of 45 mm. diameter. The orifice was 1·04 mm. diameter:

Table XXI.

Rate of flow of hydrogen, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.
12·0	50	584°
12·6	70	589
14·0	50	593
14·0	150	589

Experiments in the Widest Apparatus.—The diameter of the rough porcelain tube was 90 mm.:

Table XXII.

Rate of flow of hydrogen, c.c. per min.	Ignition-temperature.
115	594°
115	593

These results show that the ignition-temperature of hydrogen is the same in air as in oxygen.

Ignition-temperature of Carbon Monoxide in Oxygen.

Experiments in the Narrow Tube (diameter = 20 mm.).—The following results were obtained with gases dried with sulphuric acid:

Table XXIII.

Diameter of orifice, mm.	Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
0·67	11·6	15	691°	692° mean
0·67	11·6	29	691	
0·67	12·4	23	693	
0·67	13·6	27	694	
0·67	20·0	44	689	
0·67	26·5	36	695	
0·67	40·0	53	694	

When the gases were saturated with moisture at 17—18°, the following set of somewhat lower numbers was obtained:

Table XXIV.

Diameter of orifice, mm.	Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
2·12	4·6	28	No ignition	
2·12	8·0	31	677°	
2·12	11·5	34	674	665° mean
2·12	12·0	45	664	
2·12	12·0	62	677	
2·12	14·2	41	667	
2·12	17·2	33	650	
2·12	18·6	47	666	
2·12	21·0	57	665	
2·12	23·7	50	661	
2·12	27·0	45	664	
2·12	30·0	71	667	
2·12	36·5	41	664	
2·12	36·5	50	663	

Diameter of orifice, mm.	Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
0·67	4·6	50	697°	
0·67	6·4	41	683	
0·67	11·5	26	658	663° mean
0·67	13·6	53	669	
0·67	14·2	60	675	
0·67	16·4	49	661	
0·67	26·5	50	659	
0·67	35·0	57	657	
0·67	49·5	50	660	

As in the case of hydrogen, the ignition-temperature of carbon monoxide diminishes as the rate of the stream is increased. When the rate exceeds 10 c.c. per minute, a fairly constant ignition-temperature is found. For the moist gases a mean temperature of 664° was found: this was raised to 692°, when both gases were passed through sulphuric acid.

Experiments in the Wider Apparatus (diameter=45 *mm.).*—The following experiments with moist gases were performed with an orifice of 1·70 mm. diameter:

TABLE XXV.

Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
12	56	674°	
21	51	653	
21	51	646	
21	51	646	
21	51	646	
21	56	658	
21	56	651	
21	56	653	650° mean
26	64	646	
26	64	656	
26	64	660	
26	64	648	
34	56	637	
39	64	646	

A result is observed in the case of carbon monoxide similar to that obtained for hydrogen, namely, a slightly lower ignition-temperature in a wider tube. The results found lie between 637° and 660°, with a mean of 650°.

Ignition-temperature of Carbon Monoxide in Air.

The results obtained in a porcelain tube, 20 mm. diameter, with moist gases were:

TABLE XXVI.

Diameter of orifice, mm.	Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.	
2·12	5·4	34	698°	
2·12	6·8	44	691	
2·12	12·0	28	664	
2·12	15·0	50	658	
2·12	15·8	40	671	
2·12	17·2	40	653	
2·12	24·5	47	667	
2·12	40·0	78	645	662° mean
2·12	44·5	50	666	
0·67	16·7	75	661	
0·67	26·5	50	663	
0·67	33·0	50	669	

Experiments in the Wider Tube (*diameter*=45 *mm.*).—Moist gases:

TABLE XXVII.

Rate of flow of carbon monoxide, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.	
21	56	658°	651° mean.
21	56	656	
41	56	646	
41	56	644	

In these experiments a faint blue haze appeared just previous to ignition.

The results for carbon monoxide and air are quite parallel to those for carbon monoxide in oxygen; the ignition-temperature of carbon monoxide in air lies between the same limits.

Ignition-temperature of Cyanogen in Oxygen.

These experiments were performed with a quartz nozzle in an outer porcelain tube of 22 mm. diameter:

TABLE XXVIII.

Rate of flow of cyanogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
5	38	845°	849° mean.
6	25	828	
6	25	825	
6	38	864	
6	38	857	
6	49	847	
6	49	841	
10	29	823	
10	29	826	
10	49	846	
10	49	854	
10	82	880	
10	82	880	
15	49	844	
15	49	833	
15	82	871	
15	82	869	
20	70	859	
20	70	861	

Ignition was accompanied by a sharp report, louder in those cases where the rate of flow of oxygen was slower. The numbers found lie within the limits 820—880°, with a mean of 849°.

The following results were obtained in the 45 mm. apparatus:

TABLE XXIX.

Rate of flow of cyanogen, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
9·7	43	803°	811° mean.
9·7	86	818	
18·0	41	806	
18·0	86	810	
29·6	86	817	

Ignition-temperature of Cyanogen in Air.

The following results were obtained in the 45 mm. apparatus:

TABLE XXX.

Rate of flow of cyanogen, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.	
5·5	150	853°	856° mean.
5·5	200	862	
9·7	200	850	
18·0	200	858	

Ignition-temperature of Ethylene in Oxygen.

The ethylene was obtained from alcohol and sulphuric acid, the evolved gas being washed and finally purified by liquefaction and fractional distillation several times repeated. It was stored over glycerol and water, and dried by calcium chloride.

Diameter of porcelain tube 20 mm., of orifice 0·99 mm. The rate of flow of oxygen was about 70 c.c.:

TABLE XXXI.

Rate of flow of ethylene, c.c. per min.	Ignition-temperature.	
0·5	666°	Crackling ignition
1·4	616	,, ,,
1·4	627	,, ,,
1·7	626	,, ,,
2·2	610	,, ,,
2·4	595	,, ,,
2·7	591	,, ,,
3·6	575	,, ,,
3·6	539	,, ,,
4·8	537	Moderate explosion
6·5	536	,, ,,
6·7	559	,, ,,
6·7	555	,, ,,
9·5	532	Loud explosion

These results show a gradual decrease in ignition-temperature with increasing rates of flow of ethylene.

Diameter of porcelain tube 45 mm., of orifice 1·70 mm.

TABLE XXXII.

Rate of flow of ethylene, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.		
12	40	563°		Quiet ignition
12	40	560		,, ,,
12	60	560		,, ,,
12	90	560		,, ,,
12	90	558		Loud ignition
12	110	551		,, ,,
12	150	553		,, ,,
12	200	555		,, ,,
15	40	538 (twice)		,, ,,
15	60	540		Louder ignition
15	110	531		,, ,,
15	150	521		,, ,,
15	200	516		,, ,,
20	40	507		,, ,,
20	64	514		,, ,,
20	99	508		,, ,,
20	150	519		,, ,,
20	200	519	510°	,, ,,
30	40	500	mean	Very loud ignition
30	75	500		,, ,,
30	99	511		,, ,,
30	150	511		,, ,,
30	200	511		,, ,,

With a stream of ethylene not slower than 20 c.c. per minute, the ignition-temperature of ethylene in oxygen was found to lie between 500° and 519°, with a mean of 510°.

Ignition-temperature of Ethylene in Air.

These experiments were performed under the same conditions as those shown in the last table for ethylene in oxygen, and are therefore strictly comparable with them:

TABLE XXXIII.

Rate of flow of ethylene, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.	Rate of flow of ethylene, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.
12	64	542°	15	200	543°
14	110	530	20	110	542
12	150	537	20	150	542
12	200	548	20	200	543
15	64	529	30	140	547
15	150	531	30	200	543

These results lie between 529° and 548°: with a stream of ethylene not slower than 20 c.c. per minute the temperatures lie between 542° and 547°, with a mean of 543°.

Ignition-temperature of Acetylene in Oxygen.

Acetylene was obtained from calcium carbide and water, the resultant gas being purified by passage through towers containing ferric, cupric, and cuprous chlorides.

In the narrowest apparatus (20 mm.), the rates of flow of acetylene could not be increased beyond 5·8 c.c., owing to the violence of the explosions.

TABLE XXXIV.

Rate of flow of acetylene, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
0·6	50 (approx.)	—	No ignition at 692°.
1·9	50 ,,	527°	Crackling explosion.
2·2	50 ,,	523	,, ,,
2·4	50 ,,	498	,, ,,
2·9	50 ,,	506	Very noisy explosion.
5·8	50 ,,	452	,, ,,

It was found possible to proceed considerably beyond this rate of flow of acetylene in the wider tube (diameter 45 mm.):

TABLE XXXV.

Rate of flow of acetylene, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.		
7	43	501°		Noisy ignition.
7	70	508		,, ,,
7	110	512		,, ,,
7	200	545		,, ,,
14	60	437	440°	Loud ignition
14	110	443		
14	200	479		,, ,,
19·5	140	416	417	Violent ignition.
19·5	200	418		

The ignition-temperature is lowered by increase in the rate of supply of acetylene, but these numbers do not point very definitely to any lower limit. We might, however, put forward tentatively the numbers 416—440° (with a mean of 428°) as at least an approximation to the truth.

Ignition-temperature of Acetylene in Air.

In the wider tube (45 mm.), the force of the ignition was so moderated by the use of air that rates up to 30 c.c. per minute of acetylene could be employed:

TABLE XXXVI.

Rate of flow of acetylene, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.		
8	60	546°		Quiet ignition.
8	100	545		,, ,,
8	100	565		,, ,,
8	200	540		,, ,,
8	200	540		,, ,,
13	64	453		Loud ignition.
13	110	469		,, ,,
13	200	483		,, ,,
13	200	477		,, ,,
23	125	433	429° mean.	Louder ignition.
23	200	440		,, ,,
23	200	435		,, ,,
25	90	429		,, ,,
25	140	429		,, ,,
25	200	440		Very loud ignition.
30	110	406		,, ,,
30	200	419		,, ,,

The ignition-temperature is thus found to be fairly constant between 406° and 440°, with a mean of 429°, when the stream of acetylene is not slower than 20 c.c. per minute. This mean is in fair agreement with the ignition-temperature in oxygen.

Ignition-temperature of Hydrogen Sulphide in Oxygen.

Pure hydrogen sulphide was obtained from stibnite and hydrochloric acid, with subsequent liquefaction of the gas evolved. It was stored over mixed glycerol and water in a glass gasholder, from which it could be passed through a water bubbler for measurement of its rate of flow. Before entering the furnace it was roughly dried by calcium chloride. The diameter of the porcelain tube was 20 mm. Quartz nozzles were employed:

TABLE XXXVII.

Diameter of orifice, mm.	Rate of flow of H_2S, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
2·12	4·5	90	232°	230° mean.
2·12	9	90	229	
2·12	13	36	225	
2·12	13	36	225	
2·12	13	40	227	
2·12	13	82	234	
2·12	14	90	232	
2·12	19·5	90	235	
2·12	24	62	229	
0·67	8·7	75	232	

In experiment 9 there was such a violent explosion that it was deemed inexpedient to use greater rates of hydrogen sulphide.

It was observed that just before ignition copious fumes were evolved from the apparatus, and some sulphur was deposited at the top of the furnace tube, showing that much oxidation had occurred.

Experiments with Wider Furnace.—The diameter of the porcelain tube was 45 mm. A glass nozzle with an orifice of 1·70 mm. diameter was used:

TABLE XXXVIII.

Rate of flow of H_2S, c.c. per min.	Rate of flow of oxygen, c.c. per min.	Ignition-temperature.	
10	40	—	Slow combustion without ignition.
10	99	—	
22	90	233°	227° mean
22	90	223	
22	200	221	
22	200	220	
30	110	220	
30	140	226	
30	200	235	
43	110	226	
43	150	235	
43	200	231	

The results of this set of experiments are, on the whole, slightly lower than those of the previous set. Both sets show, as a rule, that a higher rate of flow of oxygen caused a somewhat higher ignition-temperature; but it is impossible to work within very wide ranges of oxygen supply, for, unless there is a fairly large excess of oxygen in the tube, the process of slow combustion prevents ignition.

The ignition-temperature may be placed at 220—235°.

Ignition-temperature of Hydrogen Sulphide in Air.

Diameter of porcelain tube, 20 mm. Diameter of the orifice, 0·67 mm.

TABLE XXXIX.

Rate of flow of H_2S, c.c. per min.	Rate of flow of air, c.c. per min.	Ignition-temperature.	
4·5	99	375°	
4·5	99	383	
6·0	140	357	
8·0	140	363	
8·3	19	—	No ignition below 570°
9·0	90	—	,, ,, 400
10·5	87	—	,, ,, 400
10·5	150	358	364° mean
10·5	180	364	
11·0	180	366	
12·4	140	346	
17·0	180	371	
40·0	250	379	

In these experiments copious fumes were evolved, and sulphur was deposited below the ignition-temperature. The results are about 140° higher than the corresponding experiments in oxygen. It will be observed, however, that the rate of supply of air has to be fairly large in order to cause ignition, and to see if these large rates of air would account for the difference in ignition-temperatures, an experiment was performed with hydrogen sulphide and oxygen flowing at the rates 10·5 and 250 c.c. per minute respectively. The result was an elevation of ignition-temperature of about 45°, much less than the elevation caused by air flowing at an even less rate.

Experiments in the Wider Tube.—Experiments in the apparatus with porcelain tube of 45 mm. diameter failed to give ignition on account of the slow oxidation of the hydrogen sulphide, as shown by the production of fumes and deposition of sulphur.

Ignition-temperature of Methane in Oxygen.

Experiments in the Narrow Apparatus (22 *mm.*).—Several sets of experiments were performed, the result of which was to show that the ignition-temperature depended on conditions which did not affect that of hydrogen, namely, the rates of flow of both gases. With methane flowing at rates from 10 to 30 c.c. per minute, and oxygen from 50 to 200 c.c., a lower ignition-temperature was obtained by either increasing the rate of methane or decreasing the rate of oxygen. The minimum was 556°, all the numbers lying between the rounded figures 550° and 670°.

Experiments in the Medium Apparatus (45 *mm.*).—In these experiments, with similar rates of flow of the gases, the limits were 590—700°. It was peculiar that methane showed a decidedly higher ignition-temperature in the wider tube than in the narrow one. More remarkable is the fact that an increase in the rate of supply of oxygen lowered the ignition-temperature appreciably, instead of raising it as occurred in the narrow tube.

These facts must be connected in some way with either the influence of surface or the excessive amount of oxidation which proceeds before the ignition-temperature is reached. It is, of course, difficult to say whether the ignition which took place ultimately was really the ignition of methane itself or of some product of its incomplete oxidation. All we may say is that when a jet of methane issued into an atmosphere of oxygen, ignition occurred between the limits, somewhat ill-defined, of 550° and 700°.

Ignition-temperature of Methane in Air.

The numbers obtained in several sets of experiments in both the narrow and the wider tubes gave results about 50—100° higher than the corresponding ones with air. They lay between 650° and 750°.

Ethane.

The ignition-temperature of ethane depended, like that of methane, on the rates of flow of the gases, and in just the same way as methane on the diameter of the porcelain tube. The results in the narrow tube lay between 520° and 630°; in the wider tube between 560° and 630°, for oxygen. For air the same limits were found.

Propane.

The results obtained with propane and oxygen showed the same general character as those with methane and ethane. The result of seventeen experiments was an ignition-temperature between 490° and 570°.

Ammonia.

The smallest furnace was employed, with a quartz nozzle and thermo-junction cover. Ammonia ignited easily in a large excess of oxygen, with production of much nitric acid. A trace of the latter was found in the gases issuing from the tube at temperatures just below the ignition-temperature. Increasing the rate of flow of either the ammonia or the oxygen caused a fall in the ignition-temperature. Roughly, it was within the limits 700° to 860°.

The authors desire to thank Miss Florence Wilkinson for assistance in the earlier stages of the work, and Mr. D. Tyrer for similar service in the latter stages.

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LXVIII.—*Studies in Asymmetric Synthesis. Part VII. The Influence of the* d-*Amyl Group.*

By Alex. McKenzie and Hermann August Müller.

The optically active compounds which have been employed hitherto in the course of this series of experiments on asymmetric synthesis are *l*-menthol, *l*-borneol, and *d*-borneol. Of the two former alcohols, *l*-menthol is the more strongly lævorotatory, and it appears from a consideration of those cases where an asymmetric synthesis of the same compound has been effected both by *l*-menthol and by *l*-borneol that the extent of this synthesis is more pronounced when *l*-menthol is used. Thus a mixture of *r*- and *l*-atrolactinic acids with $[\alpha]_D$ $-9{\cdot}5^\circ$ in ethyl-alcoholic solution was obtained from magnesium methyl iodide and *l*-menthyl benzoylformate (Trans., 1904, **85**, 1249). On the other hand, when *l*-bornyl benzoylformate was substituted for the menthyl ester, the activity of the resulting atrolactinic mixture was much less, namely, $[\alpha]_D$ $-1{\cdot}9^\circ$ in ethyl-alcoholic solution (Trans., 1906, **89**, 365). In a similar manner, a mixture of *r*- and *d*-atrolactinic acids with $[\alpha]_D$ $+5{\cdot}4^\circ$ in ethereal solution was obtained from magnesium phenyl bromide and *l*-menthyl pyruvate (Trans., 1906, **89**, 365), whereas when *l*-bornyl pyruvate was used, the atrolactinic acid mixture was only slightly dextrorotatory (Trans., 1906, **89**, 688).

In the work recorded in the present paper, the question as to the directing influence, if any, which would be exerted by an active grouping of slight optical activity, such as the *d*-amyl group, has been investigated. *d*-Amyl alcohol * has $[\alpha]_D^{20}$ $-5{\cdot}90^\circ$ (Marckwald and McKenzie, *Ber.*, 1901, **34**, 485), and is thus much less active than either menthol or borneol. The action of various Grignard reagents on *d*-amyl pyruvate and *d*-amyl benzoylformate was examined, and the asymmetric syntheses of substituted glycollic acids were, as we had anticipated, extremely slight. The reduction of *d*-amyl pyruvate by aluminium amalgam led to the asymmetric synthesis of *d*-lactic acid. The asymmetric synthesis of *l*-lactic acid by the reduction of *l*-menthyl pyruvate and *l*-bornyl pyruvate has already been described (Trans., 1905, **87**, 1373; 1906, **89**, 688).

All the evidence which has been accumulated up to this point undoubtedly points to the conclusion that the more optically active is the directing asymmetric agent the more pronounced is the asymmetric synthesis.

---

* Marckwald (*Ber.*, 1902, **35**, 1599) suggests the nomenclature *d*-amyl alcohol for the lævorotatory amyl alcohol present in fusel oil. It forms dextrorotatory derivatives, and is converted into *d*-valeric acid on oxidation.

EXPERIMENTAL.

Action of Magnesium Organic Compounds on d-*Amyl Pyruvate.*

d-*Amyl pyruvate*, $CH_3\cdot CO\cdot CO_2\cdot C_5H_{11}$, prepared from pyruvic acid, *d*-amyl alcohol, and sulphuric acid according to the Fischer-Speier method of esterification, is a colourless oil, which boils at 81—82°/10 mm., and has D^{13}_{4} 0·9724 :

0·2064 gave 0·4562 CO_2 and 0·1642 H_2O. C = 60·3 ; H = 8·9.

$C_8H_{14}O_3$ requires C = 60·7 ; H = 8·9 per cent.

In a 50 mm. tube its rotation was α^{13}_{D} $+2·28°$; whence $[\alpha]^{13}_{D}$ $+4·7°$.

When this ester (12 grams, 1 mol.) was acted on by magnesium phenyl bromide (1¼ mols.), the resulting phenylmethylglycollic acid did not exhibit any appreciable optical activity. Similarly, no asymmetric synthesis took place under the conditions employed when magnesium α-naphthyl bromide was substituted for the phenyl bromide. A very slight asymmetric synthesis was, however, observed when magnesium ethyl iodide was used. The methylethylglycollic acid prepared from the Grignard reagent (2 mols.) and the ester (7 grams, 1 mol.) was feebly dextrorotatory.

Reduction of d-*Amyl Pyruvate. Asymmetric Synthesis of* d-*Lactic Acid.*

A solution of 15 grams of *d*-amyl pyruvate in 100 c.c. of moist ether was added to 15 grams of aluminium amalgam. After three days, fresh aluminium amalgam was added, together with a little water, and the mixture allowed to remain at the laboratory temperature for three days longer. The ethereal solution was drained off and the residue washed with ether. The product obtained after removal of the ether was hydrolysed by shaking at the ordinary temperature for one hour with 360 c.c. of an aqueous solution of potassium hydroxide containing 7·2 grams of alkali. The active amyl alcohol was then completely separated from the aqueous solution of potassium salt by steam distillation and subsequent evaporation of the aqueous solution. After acidification with sulphuric acid, the lactic acid was extracted with ether by means of a continuous extraction apparatus. The ether was expelled, water added to the resulting syrup, and the aqueous solution (20 c.c.) polarimetrically examined. It was dextrorotatory, 16 c.c. giving α^{18}_{D} $+0·38°$ in a 2-dcm. tube. The aqueous solution was then neutralised by sodium carbonate, and the solution of sodium salt evaporated to 20 c.c. This was lævorotatory, 16 c.c. giving $\alpha_D - 0·28°$ in a 2-dcm. tube, and became dextrorotatory on acidification.

The result was confirmed by a second experiment.

Action of Magnesium Organic Compounds on d-*Amyl Benzoylformate.*

d-*Amyl benzoylformate*, $C_6H_5\cdot CO\cdot CO_2\cdot C_5H_{11}$, prepared from benzoylformic acid, *d*-amyl alcohol, and sulphuric acid according to the Fischer-Speier method of esterification, is a colourless oil, which boils at 163°/16 mm., and has D_4^{19} 1·050:

0·1617 gave 0·4203 CO_2 and 0·1093 H_2O. C = 70·9; H = 7·6.

$C_{13}H_{16}O_3$ requires C = 70·9; H = 7·3 per cent.

In a 1-dcm. tube its rotation was α_D + 4·26°; whence $[\alpha]_D^{19}$ + 4·1°.

An ethereal solution of magnesium methyl iodide ($1\frac{1}{4}$ mols.), prepared from 1·25 grams of magnesium, 7·2 grams of methyl iodide, and 30 c.c. of ether, was gradually added within an interval of forty minutes to a solution of 9 grams of *d*-amyl benzoylformate (1 mol.) in 30 c.c. of ether. After twenty-two hours at the laboratory temperature, the mixture was boiled for forty-five minutes, and then decomposed by ice and sulphuric acid. The resulting ester mixture was hydrolysed by heating for two and a-half hours with 100 c.c. of ethyl-alcoholic potassium hydroxide containing 3 grams of alkali. The bulk of the ethyl alcohol was removed by evaporation, water added, and the active amyl alcohol completely expelled by steam distillation. The aqueous solution of potassium salt, after neutralisation of the free alkali present, could not be sufficiently decolorised by charcoal in order to render accurate polarimetric observation possible. An excess of mineral acid was added, the organic acid extracted with ether, and the ethereal solution decolorised. In this manner a mixture (4·7 grams) of *r*-atrolactinic acid together with a very little of the *d*-acid was obtained; when dried over sulphuric acid under diminished pressure, it melted indefinitely between 82° and 88°. When dissolved in acetone and examined in a 2-dcm. tube, it gave α_D + 0·10°. The acetone was expelled, the acid neutralised by aqueous potassium hydroxide, and the solution of potassium salt then examined in a 2-dcm. tube. The rotation was α_D + 0·12°.

When *d*-amyl benzoylformate (10 grams, 1 mol.) was acted on by magnesium ethyl iodide ($1\frac{1}{2}$ mols.), the extent of the asymmetric synthesis was again exceedingly slight. The aqueous solution of potassium salt, obtained after hydrolysis of the ester mixture and removal of the lævorotatory alcohol, gave only α_D + 0·15° in a 2-dcm. tube, whilst the phenylethylglycollic acid (4 grams) obtained from it melted indefinitely between 90° and 95°, and was also distinctly dextrorotatory.

A similar result followed from the use of magnesium α-naphthyl bromide. The ester (10 grams, 1 mol.) was acted on by the Grignard reagent ($2\frac{1}{2}$ mols.) in the usual manner. The aqueous solution of potassium salt, obtained after the saponification of the ester mixture and removal of the amyl alcohol, was dextrorotatory, and on acidification yielded phenyl-α-naphthylglycollic acid (3·9 grams), which gave α_D +0·16° when dissolved in acetone and examined in a 2-dcm tube. The acid was converted into potassium salt, the aqueous solution of which gave α_D +0·16° in a 2-dcm. tube.

Amyl Esters of Gallic Acid.

The *d*-amyl alcohol (2-methylbutanol-1),

$$CH_3\cdot CH(CH_2\cdot OH)\cdot CH_2\cdot CH_3,$$

which was used for the preparation of the esters of pyruvic and benzoylformic acids, was prepared as described by Marckwald and McKenzie (*loc. cit.*), who were the first to isolate it from fusel oil. This method involves the preparation of 1-*d*-amyl-3-nitrophthalic acid. The process is somewhat tedious, since the separation from the isomeric 1-*iso*amyl-3-nitrophthalic acid must be effected, and this is slow owing to the formation of mixed crystals.

Attempts were made to prepare the active alcohol for use in the present investigation by substituting gallic acid for 3-nitrophthalic acid. Gallic acid forms crystalline esters both with *d*-2-methylbutanol-1 and *iso*amyl alcohol, $(CH_3)_2CH\cdot CH_2\cdot CH_2\cdot OH$ (2-methylbutanol-4), and has the further advantage of being monobasic. The experiments were not, however, successful. *d*-Amyl gallate could not be isolated from its mixture with *iso*amyl gallate owing to the formation of mixed crystals; the method of separating mixed crystals, which was successfully employed by Marckwald and McKenzie, failed in this case. A number of observations were made regarding the amyl gallates, and these may be recorded here.

For the preparation of *iso*amyl gallate, *iso*amyl alcohol was isolated from Kahlbaum's pyridine-free amyl alcohol according to the method of Marckwald and McKenzie. Gallic acid was deprived of its water of crystallisation and esterified by means of the inactive alcohol, using hydrogen chloride.

iso*Amyl gallate*, $C_6H_2(OH)_3\cdot CO_2\cdot C_5H_{11}$, crystallises from water in colourless, long, silky needles and melts at 145—146°. For analysis, a specimen was crystallised from chloroform:

0·1769 gave 0·3891 CO_2 and 0·1064 H_2O. C = 60·0; H = 6·7.

$C_{12}H_{16}O_5$ requires C = 60·0; H = 6·7 per cent.

The ester is very slightly soluble in water, and undergoes practically no hydrolysis when heated with water. It is sparingly soluble in benzene, light petroleum, or chloroform; it is very soluble in ethyl alcohol or ether.

It can also be prepared, although not readily, from commercial amyl alcohol. In one experiment, carried out by Mr. G. H. Martin in this laboratory, an alcohol with α_D $-2·14°$ $(l=2)$ was taken, and in this case 25 crystallisations, conducted with aqueous ethyl alcohol, were necessary before the separation of the *iso*amyl ester from the mixed crystals was complete. The ester obtained after this treatment gave the inactive *iso*amyl alcohol on hydrolysis. This method of preparing *iso*amyl alcohol is not nearly so convenient as that involving the use of 3-nitrophthalic acid.

*iso*Amyl gallate has already been described by Ernst and Zwenger (*Annalen*, 1871, **159**, 27) as melting at 139°, but it is certain that these authors did not obtain the ester free from its active isomeride.

For the preparation of *d*-amyl gallate, the *d*-alcohol was prepared according to the method of Marckwald and McKenzie. Dried gallic acid was esterified by means of this alcohol and hydrogen chloride.

d-*Amyl gallate*, $C_6H_2(OH)_3·CO_2·C_5H_{11}$, separates from chloroform or benzene in colourless, silky needles and melts at 108—109°. It resembles its isomeride in appearance and solubility.

0·2254 gave 0·4951 CO_2 and 0·1401 H_2O. $C=59·9$; $H=6·95$.

$C_{12}H_{16}O_5$ requires $C=60·0$; $H=6·7$ per cent.

Its rotation was determined in acetone solution:

$$l=1,\ c=10,\ \alpha_D^{17}\ +0·40°,\ [\alpha]_D^{17}\ +4·0°.$$

When the esterification of gallic acid was conducted with a mixture of *d*-amyl and *iso*amyl alcohols having α_D^{17} $-7·65°$ $(l=2)$, the unesterified portion of the alcohol gave α_D^{17} $-7·76°$ $(l=2)$. The solid product, obtained after removal of the unesterified gallic acid and amyl alcohol, was crystallised once from a large amount of water, after which treatment it melted at 115—117°. It was then crystallised eleven times from dry chloroform until the melting point was sharp, namely, 119—120°. A determination of the specific rotation of this product in acetone solution showed, however, that it was not homogeneous, a conclusion which was also arrived at from the fact that its melting point was different from that of the pure active ester. The activity was $[\alpha]_D^{17}$ $+3·7°$ for $c=10·11$ in acetone solution. The alcohol obtained by the hydrolysis of this product gave the value α_D^{17} $-8·02°$ $(l=2)$, whereas the pure *d*-alcohol has α_D^{20} $-9·62°$ $(l=2)$.

When the esterification of gallic acid was conducted with an alcohol having α_D^{18} $-9·03°$ $(l=2)$, the product obtained after ten crystallisations from chloroform and five subsequent crystallisations from benzene melted at 119—120° and also consisted of mixed crystals.

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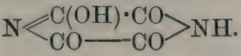
LXIX.—*Tetraketopiperazine. Part II.*

By Alfred Theophilus de Mouilpied and Alexander Rule.

The preparation and some of the reactions of tetraketopiperazine have already been described by the authors (Trans., 1907, **91**, 176). Its behaviour towards alkalis and phenylhydrazine showed that its constitution was probably represented by the formula



$$\mathrm{N}\!\begin{smallmatrix}\diagup\\\diagdown\end{smallmatrix}\!\begin{matrix}\mathrm{C(OH)\cdot CO}\\ \mathrm{CO{-}{-}{-}CO}\end{matrix}\!>\!\mathrm{NH}.$$

Experiments have now been undertaken on the reduction of the compound, and its behaviour towards phosphorus pentachloride, aniline, and phenylcarbimide has been examined. The production of coloured compounds, which were decomposed at once by water, has been observed on various occasions, and these have been investigated.

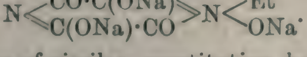
Tetraketopiperazine is very inert towards reagents, and in most cases any reaction has resulted in the decomposition of the compound. Thus it does not react with phenylcarbimide, bromine (in acetic or sulphuric acid solution), phosphorus pentachloride, phosphoryl chloride, or (as silver salt) with ethyl iodide. With tin and hydrochloric acid no action took place, but with hydriodic acid and red phosphorus the compound was entirely decomposed with the formation of oxalic acid and ammonium iodide; and sodium and amyl alcohol furnished a brilliantly coloured substance, the investigation of which is described on p. 550.

Preparation and Constitution of the Blue Compounds.

In the earlier preparations of tetraketopiperazine by the action of sodium ethoxide on oxamethane, the production of a deep blue colour was always observed, sometimes locally, sometimes throughout the mass of the product. On repeating the preparation with amyl alcohol and phenol instead of ethyl alcohol, similar coloured substances were produced.

These compounds are permanent in dry ether, and analysis showed them to be double compounds of one molecule of the salt of the tetraketone with one molecule of sodium alkyloxide.

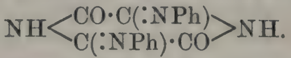
We are of the opinion that the structure previously suggested for the yellow disodium salt of the tetraketone is preserved in the blue compounds, which would therefore have the constitution



$$\mathrm{N}\!<\!\begin{matrix}\mathrm{CO\cdot C(ONa)}\\ \mathrm{C(ONa)\cdot CO}\end{matrix}\!\geqslant\!\mathrm{N}\!<\!\begin{matrix}\mathrm{Et}\\ \mathrm{ONa}\end{matrix}.$$

Coloured substances of similar constitution have been obtained by Piutti (*Gazzetta*, 1906, **36**, ii, 723).

As mentioned in the former paper, on boiling the tetraketone with aniline a white, crystalline compound is formed, which sublimes with great readiness to a voluminous, white product. Re-sublimation as a means of purification was abandoned, as it was found that some decomposition always occurred. The compound was recrystallised from methyl alcohol, and analysis showed it to be 2:5-*dianilotetraketopiperazine*,



$NH<\genfrac{}{}{0pt}{}{CO\cdot C(:NPh)}{C(:NPh)\cdot CO}>NH.$

Attempts to synthesise diphenyltetraketopiperazine by the condensation of ethyl oxalate with oxanilide in presence of sodium ethoxide were unsuccessful.

EXPERIMENTAL.

Compound of Tetraketopiperazine with Sodium Amyloxide.

Three grams of tetraketopiperazine were suspended in amyl alcohol, and sodium in small pieces, was added to the boiling mixture; at first a blue colour developed and quickly disappeared, but after the addition of more sodium the blue colour became more permanent, until a point was reached at which the whole mixture turned a brilliant blue. The boiling was continued for ten minutes in presence of excess of sodium, and the mixture was then quickly filtered. The residue was washed three times with hot absolute alcohol and transferred to a desiccator. The dry substance appeared quite homogeneous, and was dark purple in colour. For analysis it was dried at 110°:

0·0974 gave 0·0683 Na_2SO_4. Na = 22·71.

$C_4O_4N_2Na_2,C_5H_{11}ONa$ requires Na = 23·31 per cent.

$C_4O_4N_2Na_2$,, Na = 24·73 ,, ,,

The compound is immediately decomposed on the addition of water, the blue colour disappearing entirely. When the substance is kept in the air the colour slowly fades.

When kept under absolute ether it showed very little change after several months.

Compound of Tetraketopiperazine with Sodium Ethoxide.

If the tetraketone is suspended in ethyl alcohol and sodium added, as in the preceding case, a blue colour slowly develops, but disappears again on cooling. In another experiment the tetraketone was heated with sodium ethoxide in a paraffin-bath to 150°, but no blue colour was formed, the product being dark brown.

It was found impossible to prepare the sodium ethoxide additive compound from the tetraketone direct, but by carrying out the condensation of oxamethane with excess of sodium ethoxide in boiling xylene the derivative was obtained.

Oxamethane (1 mol.) was suspended in xylene, ethyl alcohol (3 mols.) added, and the mixture boiled. Sodium (3 atoms) was added in small pieces, and the first product was a yellow salt which gradually became almost black. On prolonged boiling, a blue colour gradually developed, and after about two hours the product was deep indigo-blue and showed no white specks. The mixture was filtered as rapidly as possible, washed with boiling alcohol and ether, and transferred to a flask containing absolute ether.

For analysis a portion was collected, washed with ether, and dried at 110°:

0·1342 gave 0·1136 Na_2SO_4. Na = 27·42.

$C_4O_4N_2Na_2,C_2H_5ONa$ requires Na = 27·16 per cent.

The substance appears to be the most unstable of these compounds, and even under absolute ether decomposes slowly with the separation of the yellow disodium salt.

Compound of Tetraketopiperazine with Sodium Phenoxide.

Tetraketopiperazine (1 mol.) was suspended in xylene together with phenol (3 mols.). The mixture was boiled, and sodium (3 atoms) added in small pieces. No immediate change took place, but after a short time the mixture darkened in colour and assumed a blue tint. After boiling for three hours, the mauve product was collected, washed with alcohol and ether, and dried:

0·1096 gave 0·0768 Na_2SO_4. Na = 22·84.

$C_4H_4N_2Na_2,C_6H_5ONa$ requires Na = 22·69 per cent.

The compound is very sensitive to the action of moisture, quickly becoming yellow when kept in the air.

The compound formed by the action of aniline on tetraketopiperazine has been further investigated. It sublimed readily to a voluminous, white product, which was crystallised from methyl alcohol:

0·1084 gave 0·2586 CO_2 and 0·0474 H_2O. C = 65·14 ; H = 4·85.
0·0746 ,, 18·9 c.c. N_2 (moist) at 16° and 762 mm. N = 19·07.
$C_{16}H_{12}O_2N_4$ requires CO_2 = 65·75 ; H = 4·10 ; N = 19·17 per cent.

2 : 5-*Dianilotetraketopiperazine* is insoluble in water, and when heated with potassium hydroxide, aniline is evolved. It is soluble in concentrated sulphuric acid, and is reprecipitated on treatment of the solution with water.

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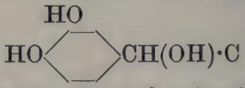
LXX.—*The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives. Part IV. Derivatives of Dihydroxyphenyl-acetic, -glycollic, and -glyoxylic Acids.*

By George Barger and Arthur James Ewins.

Derivatives of ethylcatechol have recently received much attention on account of their relationship to epinephrine (adrenaline); certain cyclic carbonates and methylene ethers belonging to this class were described a short time ago by one of us (Trans., 1908, **93**, 2081), and the same and closely related derivatives have been obtained simultaneously by Pauly (*Ber.*, 1908, **41**, 4151) and by Böttcher (*Ber.*, 1909, **42**, 253). The latter author claims to have accomplished a new synthesis of the active principle of the suprarenal gland—a claim the validity of which has been questioned by Pauly (*Ber.*, 1909, **42**, 484), not without reason.

While working at this subject we were induced to prepare other substances containing the complex  in order to compare their solubility in water with that of epinephrine, which, strangely enough for a substance of this type, is insoluble in water. In particular we attempted the preparation of the methylamide of 3:4-dihydroxymandelic acid, $C_6H_3(OH)_2\cdot CH(OH)\cdot CO\cdot NH\cdot CH_3$; we found this substance to be very soluble in water, and were unable to obtain it in the pure state. As was to be expected, it was physiologically inert, and it could not be reduced to a physiologically active base.

The above amide was prepared from the corresponding ethyl ester, which we isolated in a pure crystalline condition. It is readily soluble in water or alcohol, and dihydroxymandelic acid itself is extremely soluble, in contrast to epinephrine.

The starting point of our experiments was the observation that, although 3:4-methylenedioxymandelic acid itself can only be prepared in small quantities by the method given by Lorenz (*Ber.*, 1881, **14**, 793), a good yield of the corresponding ethyl ester is directly obtainable from piperonalcyanohydrin. From this ester we prepared the acid, and from the latter by phosphorus pentachloride the acid chloride, $CCl_2\!:\!O_2\!:\!C_6H_3\cdot CHCl\cdot COCl$, which could be easily purified by distillation. By treatment with formic acid, the cyclic carbonate of 3:4-dihydroxyphenylchloroacetic acid, $CO\!:\!O_2\!:\!C_6H_3\cdot CHCl\cdot CO_2H$, resulted, which, on boiling with water, was converted into 3 : 4-dihydroxymandelic acid.

The ethyl ester could not be readily prepared from the acid ; in order to obtain it, we utilised an observation, that when ethyl 3 : 4-methylenedioxymandelate is heated with only three molecular proportions of phosphorus pentachloride at comparatively low temperatures, scarcely any acid chloride is formed, the ester grouping remaining intact. In this way we obtained, by a series of reactions analogous to those already described, ethyl 3 : 4-dihydroxymandelate in a pure condition. Like homoprotocatechuic acid, this ester contains three hydroxyl groups, is readily soluble in water, and but sparingly so in boiling xylene ; 3 : 4-dihydroxymandelic acid contains four hydroxyl groups, is quite insoluble in boiling xylene, and extremely soluble in water.

In some of our experiments with phosphorus pentachloride (as well as with thionyl chloride) at a higher temperature (180—200°), we observed the partial conversion of the derivatives of dihydroxyphenylchloroacetic acid into derivatives of dihydroxyphenyldichloroacetic acid ; whilst the former could be converted into derivatives of dihydroxyphenylglycollic acid, the latter ultimately yielded dihydroxyphenylglyoxylic acid, $C_6H_3(OH)_2{\cdot}CO{\cdot}CO_2H$. The methylene ether of this acid had been previously obtained by the oxidation of safrole ; we prepared it more conveniently by oxidising the corresponding hydroxy-acid. Its methylamide, $CH_2{:}O_2{:}C_6H_3{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_3$, was also obtained by condensing piperonyl chloride with methyl *iso*cyanide.

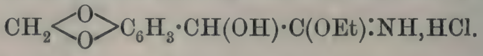
The formation of derivatives of phenyldichloroacetic acid from those of phenylmonochloroacetic acid by means of phosphorus pentachloride, referred to above, is quite analogous to the oxidation of piperonyloin (a benzoin derivative) to dicarbonyltetraoxybenzil, previously described by us (Trans., 1908, **93**, 736) as the result of the action of thionyl chloride ; in either case the grouping $CH(OH){\cdot}CO$ is oxidised to $CCl_2{\cdot}CO$.

We may here review the conditions under which the various chlorine atoms introduced by phosphorus pentachloride (and thionylchloride) are eliminated from the compounds described in this and in previous papers. The chlorine atoms in the methylene group, and in aliphatic carboxyl groups, are the most labile, and are removed by formic acid without boiling, and by exposure to moist air in the cold. The chlorine atom in 3 : 4-carbonyldioxybenzoyl chloride is somewhat more stable, and is only removed by boiling with formic acid for a short time (Trans., 1908, **93**, 568).

Next in order of stability come apparently the pair of chlorine atoms in an aldehyde group, as in 3 : 4-carbonyldioxybenzylidene chloride, which require boiling with formic acid for some time (Pauly, *Ber.*, 1907, **40**, 3096). The removal of the two chlorine atoms, which gives rise to a diketone (Trans., 1908, **93**, 737) or a ketonic acid (the present paper), is only accomplished slowly by prolonged boiling with formic acid. Finally, the single chlorine atom replacing an alcoholic hydroxyl group (Trans., 1908, **93**, 2084, and the present paper) is quite resistant to boiling formic acid, and has to be eliminated by water.

EXPERIMENTAL.

3 : 4-*Methylenedioxyphenylhydroxyacetimino-ethylether Hydrochloride*,

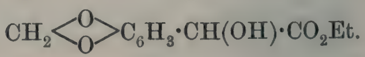

$CH_2\left<{}^{O}_{O}\right>C_6H_3\cdot CH(OH)\cdot C(OEt){:}NH,HCl.$

Piperonal (20 grams) is melted, and a concentrated solution of sodium hydrogen sulphite (15 grams) in warm water is stirred in. The additive compound which separates out is collected, washed, and made into a thick paste with a little water. A cold aqueous saturated solution of potassium cyanide (10 grams) is then added; on stirring, the bisulphite compound dissolves completely, and the piperonalcyanohydrin separates as a colourless liquid, which soon becomes pink. It is dissolved in ether, the ethereal solution is filtered, and dried. After the addition of rather more than one molecular proportion of alcohol, the solution is saturated with hydrogen chloride at a temperature below 10°. On standing for a short time, the solution is transformed into a mass of crystals. After draining and washing with dry ether, the pure hydrochloride is obtained. It melts and decomposes at 118—119°. Yield = 60 per cent. of the theoretical:

0·2067 gave 0·1104 AgCl. Cl = 13·3.

$C_{11}H_{14}O_3NCl$ requires Cl = 13·7 per cent.

Ethyl 3 : 4-*Methylenedioxymandelate*,

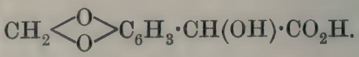

$CH_2\left<{}^{O}_{O}\right>C_6H_3\cdot CH(OH)\cdot CO_2Et.$

The hydrochloride described above is warmed with water. The ester separates as an oil which solidifies on cooling. When crystallised from xylene it forms white needles melting at 72° and boiling at 179—181°/8 mm., 197°/15 mm. The yield is almost quantitative:

0·1631 gave 0·3499 CO_2 and 0·0786 H_2O. C = 58·5; H = 5·4.

$C_{11}H_{12}O_5$ requires C = 58·9; H = 5·4 per cent.

3 : 4-*Methylenedioxymandelic Acid*,


$CH_2\left<{}^{O}_{O}\right>C_6H_3\cdot CH(OH)\cdot CO_2H.$

Ten grams of the above ester were boiled for three hours with 10 grams of potassium hydroxide dissolved in 100 c.c. of 90 per cent.

alcohol. The resulting solution was nearly neutralised with hydrochloric acid and filtered from precipitated potassium chloride. The filtrate was evaporated to dryness, and the residue dissolved in a little water. On acidification, the acid separated out and, after recrystallisation from dilute alcohol, formed colourless, hexagonal plates, melting at 162°. Yield, 80—90 per cent. The acid is only very sparingly soluble in benzene. We are unable to confirm Lorenz's statement that the substance is very unstable ; his substance cannot have been pure, as he gives the melting point 152—153° : Garelli gives 156°.

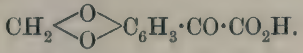
3 : 4-*Methylenedioxymandelamide*, $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CH(OH)\cdot CO\cdot NH_2$.

This substance was prepared by leaving the ester in contact with a large excess of concentrated aqueous ammonia, when it was gradually transformed into glistening, rhombic plates, which, after recrystallisation from a mixture of ethyl acetate and alcohol, melted sharply at 140°. The amide is readily soluble in hot water :

0·2196 gave 14·2 c.c. N_2 (moist) at 25° and 764 mm. N = 7·3.

$C_9H_9O_4N$ requires N = 7·2 per cent.

The reduction of this amide to a base was attempted without success.



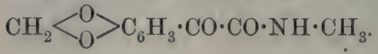
3 : 4-*Methylenedioxyphenylglyoxylic Acid*, $CH_2{<}\substack{O\\O}{>}C_6H_3\cdot CO\cdot CO_2H$.

This acid has been previously obtained by Ciamician and Silber (*Ber.*, 1890, **23**, 1165) by oxidation of *iso*safrole, but the yield is very small. We failed to obtain it from 3 : 4-methylenedioxymandelic acid by oxidation with potassium dichromate and sulphuric acid, but with alkaline permanganate a small yield of the ketonic acid was obtainable.

Five grams of methylenedioxymandelic acid were dissolved in 150 c.c. of water by means of a slight excess of sodium carbonate, and 10 grams of finely-powdered potassium permanganate were gradually added to the boiling solution. After removal of the manganese dioxide by filtration, the solution was acidified, and the acid, which separated out somewhat slowly, was crystallised from benzene, in which it is fairly soluble. It forms yellow needles melting at 148° if the benzene of crystallisation has been driven off by previous heating at 100°. Yield, 10—20 per cent.

This acid was also obtained from its methylamide (by hydrolysis with sodium hydroxide), and then formed long, yellow needles, m. p. 148—149°. The methylamide was prepared by a different method, as follows :

3 : 4-*Methylenedioxyphenylglyoxylmethylamide*,



$$\mathrm{CH_2}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{C_6H_3\cdot CO\cdot CO\cdot NH\cdot CH_3}.$$

Equimolecular proportions of piperonyl chloride,

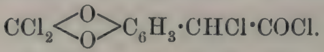
$$\mathrm{CH_2{:}O_2{:}C_6H_3\cdot COCl},$$

and methyl *iso*cyanide were heated to 90° for fifteen minutes, when the odour of the latter substance had disappeared. The resulting syrup was dissolved in chloroform, and benzene was added until no more tarry precipitate was formed. On passing steam through the yellow filtrate, a little piperonylic acid separated, and then, on cooling, a yellow oil appeared which soon solidified. After recrystallisation from very dilute sodium carbonate solution, it formed pale yellow leaflets, m. p. 112°:

0·1962 gave 11·2 c.c. N_2 (moist) at 9° and 742 mm. N = 6·70.

$C_{10}H_9O_4N$ requires N = 6·76 per cent.

3 : 4-*Dichloromethylenedioxyphenylchloroacetyl Chloride*,



$$\mathrm{CCl_2}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{C_6H_3\cdot CHCl\cdot COCl}.$$

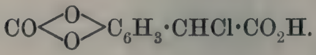
Methylenedioxymandelic acid (5 grams) was heated with four molecular proportions of phosphorus pentachloride (21·5 grams) under a reflux condenser to 180° for five hours. On distillation, phosphorus trichloride and phosphoryl chloride first passed over, and then a colourless liquid boiling constantly at 167°/10 mm., the yield of which amounted to 80 per cent. of the theory:

0·1808 gave 0·2405 CO_2 and 0·0242 H_2O. C = 36·3; H = 1·5.

0·1815 ,, 0·3430 AgCl. Cl = 46·7.

$C_9H_4O_3Cl_4$ requires C = 35·8; H = 1·3; Cl = 47·0 per cent.

3 : 4-*Carbonyldioxyphenylchloroacetic Acid*, $\mathrm{CO}<\substack{\mathrm{O}\\\mathrm{O}}>\mathrm{C_6H_3\cdot CHCl\cdot CO_2H}$.



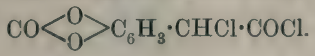
The acid chloride described above reacts violently with cold formic acid; the reaction is completed by boiling for a short time, and then a crystalline solid separates out if the solution is moderately concentrated. After recrystallisation from formic acid, the substance formed short, broad prisms melting at 144°:

0·1828 gave 0·3159 CO_2 and 0·0366 H_2O. C = 47·1; H = 2·2.

0·2041 ,, 0·1310 AgCl. Cl = 15·9.

$C_9H_5O_5Cl$ requires C = 47·3; H = 2·2; Cl = 15·5 per cent.

3 : 4-*Carbonyldioxyphenylchloroacetyl Chloride*,



$$CO<{O \atop O}>C_6H_3\cdot CHCl\cdot COCl.$$

This substance was obtained by heating the above acid (1·5 grams) with thionyl chloride (15 c.c.) on the water-bath for one and a-half hours. On distillation, the chloride boiled at 185—186°/9 mm. :

0·2102 gave 0·2458 AgCl. Cl = 28·9.

$C_9H_4O_4Cl_2$ requires Cl = 28·7 per cent.

The substance was treated in benzene solution with equimolecular proportions of various bases, but no crystalline product could be isolated.

3 : 4-*Dihydroxymandelic Acid*, $C_6H_3(OH)_2\cdot CH(OH)\cdot CO_2H$.

By warming carbonyldioxyphenylchloroacetic acid in aqueous-acetone solution on the water-bath in the presence of powdered marble, and subsequent evaporation, this acid is obtained as an amorphous, pale yellow solid, which is extremely soluble in water, alcohol, acetone, ether, or ethyl acetate, but not at all in boiling benzene or xylene. When a concentrated alcoholic solution is dropped into a large quantity of boiling xylene, the whole of the acid is at once precipitated. In spite of many attempts, we have been unable to crystallise the acid or any of its salts; the only crystalline derivative obtained was the ethyl ester described below.

A specimen purified by precipitation from alcoholic solution by benzene, and still containing a little calcium salt, was analysed, and gave, after subtracting the ash :

Found, C = 53·0 ; H = 5·9.

$C_8H_8O_5$ requires C = 52·2 ; H = 4·35 per cent.

The acid thus obtained was a white, amorphous powder, and was very unstable. Its aqueous solution darkens on exposure to light and air, instantly reduces ammoniacal silver nitrate solution, and is coloured an intense green by ferric chloride. The brucine salt of the acid separated as an amorphous precipitate on mixing alcoholic solutions of the two constituents ; the quinine salt is, on the other hand, readily soluble in alcohol. Neither salt could be crystallised.

Ethyl 3 : 4-*Dihydroxymandelate*, $C_6H_3(OH)_2\cdot CH(OH)\cdot CO_2Et$.

Ethyl methylenedioxymandelate (20 grams) was heated under a reflux condenser with three molecular proportions (55·8 grams) of phosphorus pentachloride to 160° for three hours. On distillation, a fraction boiling at 184—187°/10 mm. and weighing 19·5 grams was collected:

0·1406 gave 0·1980 AgCl. Cl = 34·8.

$C_{11}H_9O_4Cl_3$ requires Cl = 34·2 per cent.

The chlorine content and reactions of this distillate showed it to be somewhat impure *ethyl* 3 : 4-*dichloromethylenedioxyphenylchloroacetate*, $CCl_2{:}O_2{:}C_6H_3\cdot CHCl\cdot CO_2\cdot C_2H_5$; the ester grouping had remained intact. The distillate reacted violently with cold formic acid, and after distillation, 11·5 grams, boiling at 197—201°/10 mm., were collected:

0·2363 gave 0·1407 AgCl. Cl = 14·8.

$C_{11}H_9O_5Cl$ requires Cl = 13·8 per cent.

The latter substance was therefore a somewhat impure cyclic carbonate, corresponding with the first-named substance. The theoretical yield is 14 grams; the deficiency was partly due to the presence of a little acid chloride in the first distillate, which was subsequently converted by formic acid into the non-volatile acid. The second distillate, boiling at 197—201°/10 mm., consisted therefore of *ethyl* 3 : 4-*carbonyldioxyphenylchloroacetate* contaminated with a slight proportion of a substance containing more chlorine, probably the corresponding carbonyldioxyphenyldichloroacetate.

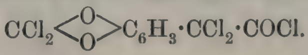
Six grams of the last-mentioned distillate were dissolved in 100 c.c. of acetone, and water was added until the solution became slightly turbid. Rather less than the calculated amount of marble was added; the solution was then boiled on the water-bath for two to three hours, after which time a turbidity was no longer produced on dilution with water. After concentration in a vacuum to 10 c.c., a pink, crystalline solid slowly separated; yield of the crude product = 70 per cent. of the theory.

Ethyl 3 : 4-*dihydroxymandelate*, which was thus obtained, is very soluble in water, but only slightly so in boiling xylene, from which it separates in white crystals melting at 152—153°:

0·1596 gave 0·3323 CO_2 and 0·0863 H_2O. C = 56·8; H = 6·0.

$C_{10}H_{12}O_5$ requires C = 56·7; H = 5·7 per cent.

3 : 4-*Dichloromethylenedioxyphenyldichloroacetyl Chloride*,



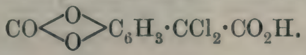
$$CCl_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_3\cdot CCl_2\cdot COCl.$$

Methylenedioxyphenylglyoxylic acid (5 grams) was heated with four molecular proportions of phosphorus pentachloride (21·6 grams) to 160° for three hours. On distillation, 5 grams of a liquid boiling at 172—187°/8 mm. were obtained; the fraction 185—187°/8 mm. was analysed:

0·1632 gave 0·3456 AgCl. Cl = 52·4.

$C_9H_3O_3Cl_5$ requires Cl = 52·7 per cent.

3 : 4-*Carbonyldioxyphenyldichloroacetic Acid*,



$$CO{<}^{O}_{O}{>}C_6H_3\cdot CCl_2\cdot CO_2H.$$

On treatment of the whole distillate with formic acid and boiling for half a minute, a white, crystalline solid separated, which was obtained pure by recrystallisation from benzene and melted at 152—153°:

0·1762 gave 0·2656 CO_2 and 0·0267 H_2O. C = 41·1 ; H = 1·7.
0·1592 „ 0·1712 AgCl. Cl = 26·6.

$C_9H_4O_5Cl_2$ requires C = 41·1 ; H = 1·5 ; Cl = 27·0 per cent.

The same acid was obtained direct from ethyl methylenedioxymandelate by the prolonged action of a large excess of thionyl chloride at a high temperature. Two grams of this ester were heated with 8 c.c. of thionyl chloride to 200° for ten hours. The excess of thionyl chloride was distilled off, and the residue then boiled at 190—225°/14 mm. On exposure to moist air in a shallow dish, the distillate partly crystallised, and after pressing on a porous plate and recrystallisation from benzene, 0·3 gram of an acid was obtained, melting at 152° and identical with 3:4-carbonyldioxyphenyldichloroacetic acid already described.

The primary result of the action of thionyl chloride on the ester was doubtless the formation of ethyl 3 : 4-carbonyldioxyphenylchloroacetate, $CO\colon O_2\colon C_6H_3\cdot CHCl\cdot CO_2Et$, boiling at 197—201°/10 mm.. described above. Two further reactions then took place; in one the ester grouping was attacked, so that the acid chloride,

$$CO\colon O_2\colon C_6H_3\cdot CHCl\cdot COCl,$$

already described b. p. 185—186°/9 mm., was formed. Finally, this was oxidised by thionyl chloride to the acid chloride,

$$CO\colon O_2\colon C_6H_3\cdot CCl_2\cdot COCl,$$

which in moist air yielded the acid $CO\colon O_2\colon C_6H_3\cdot CCl_2\cdot CO_2H$. A similarly complex distillate was obtained by the prolonged action of phosphorus pentachloride on ethyl methylenedioxymandelate at 190—200°.

Thus the fraction 170—175°/10 mm. contained Cl = 40·3; the fraction 178—184°/9 mm., Cl = 40·8; $CCl_2\colon O_2\colon C_6H_3\cdot CHCl\cdot COCl$ requires Cl = 47·0; $CCl_2\colon O_2\colon C_6H_3\cdot CHCl\cdot CO_2Et$ requires Cl = 34·2, and $CCl_2\colon O_2\colon C_6H_3\cdot CCl_2\cdot CO_2Et$ requires Cl = 42·5 per cent.

As has been pointed out above, the two additional reactions scarcely take place with phosphorus pentachloride at a lower temperature, so that the reaction product then consists almost wholly of the ester, $CCl_2\colon O_2\colon C_6H_3\cdot CHCl\cdot CO_2Et$.

3 : 4-*Dihydroxyphenylglyoxylic Acid*, $C_6H_3(OH)_2 \cdot CO \cdot CO_2H$.

This acid is readily obtained by boiling the cyclic carbonate of the corresponding dichloroacetic acid with water. The latter acid gradually dissolves, and the solution becomes yellow, carbon dioxide being evolved. On cooling, a well-crystallised solid separated, which, on recrystallisation from a mixture of ethyl acetate and petroleum (b. p. 80—90°), formed yellow needles melting at 159°. The substance retained one molecule of water of crystallisation, which it did not lose in a vacuum over sulphuric acid at the laboratory temperature; the water is, however, given off under atmospheric pressure at 100°, the substance becoming more deeply yellow.

For analysis the substance was dried by the former method:

0·0965 gave 0·1689 CO_2 and 0·0359 H_2O. C = 47·7; H = 4·1.

0·0299 lost 0·0026 H_2O at 100°. H_2O = 8·7.

$C_8H_6O_5,H_2O$ requires C = 48·0; H = 4·0; H_2O = 9·0 per cent.

3 : 4-Dihydroxyphenylglyoxylic acid is readily soluble in water, although much less than the corresponding hydroxy-acid (3 : 4-dihydroxymandelic acid, described above). The solution in water and in alcohol is coloured intensely green by ferric chloride, the coloration becoming pink on the addition of alkali.

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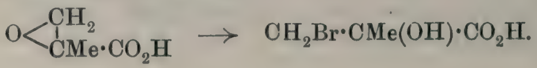
LXXI.—*The Conversion of* d-α-*Methyl*iso*serine into* d-α-*Methylglyceric Acid.*

By Francis William Kay (1851 Exhibition Scholar of the University of Manchester).

In the course of some investigations on the behaviour of β-amino-acids towards nitrosyl bromide, it was discovered that α-methyl*iso*serine (β-amino-α-hydroxy*iso*butyric acid) is converted by this reagent in the cold into β-bromo-α-methyl-lactic acid (β-bromo-α-hydroxy*iso*butyric acid):

$$NH_2 \cdot CH_2 \cdot CMe(OH) \cdot CO_2H \longrightarrow CH_2Br \cdot CMe(OH) \cdot CO_2H.$$

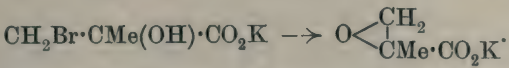
This acid has previously been described by Melikoff (*Annalen*, 1886, **234**, 213), who obtained it by the addition of hydrogen bromide to α-methylglyceric acid:



$$O{<}\begin{matrix}CH_2\\ |\\ CMe \cdot CO_2H\end{matrix} \longrightarrow CH_2Br \cdot CMe(OH) \cdot CO_2H.$$

The acid prepared from α-methyl*iso*serine melts at 102—103° and is identical in all respects with Melikoff's acid. *d*-α-Methyl*iso*serine, when submitted to the same treatment, is easily converted into the corresponding d-*β-bromo-α-methyl-lactic acid*, which crystallises from benzene in long, silky needles and melts at 114°: considerably higher than the racemic acid.

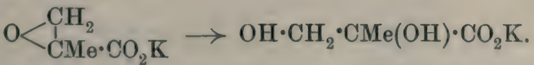
d-β-Bromo-α-methyl-lactic acid readily loses the elements of hydrobromic acid when dissolved in alcohol and treated with the theoretical amount of cold alcoholic potassium hydroxide, *potassium* d-*α-methylglycidate* being obtained as a voluminous precipitate of silky leaflets:



$$CH_2Br\cdot CMe(OH)\cdot CO_2K \longrightarrow O\!\left<\begin{matrix}CH_2\\ |\\ CMe\cdot CO_2K\end{matrix}\right.\cdot$$

Owing to the small amount of material at my disposal and the fact that α-methylglycidic acid is a syrupy substance which crystallises with the utmost difficulty, it was quite out of the question to isolate the free dextro-acid and measure its rotatory power. The potassium salt was therefore employed for the determination of the optical properties.

Now, according to the statements of Melikoff (*loc. cit.*), the potassium salt of *r*-α-methylglycidic acid readily combines with the elements of water when its aqueous solution is maintained at 95—100° for some time. This hydration leads to the formation of the potassium salt of α-methylglyceric acid, thus:



$$O\!\left<\begin{matrix}CH_2\\ |\\ CMe\cdot CO_2K\end{matrix}\right. \longrightarrow OH\cdot CH_2\cdot CMe(OH)\cdot CO_2K.$$

In order to obtain a rough estimate of the rotatory power of the *d*-modification of the latter acid (as potassium salt), the optical activity of the contents of the polarimeter tube from the previous experiment was redetermined after they had been maintained at 90° for two hours.

EXPERIMENTAL.

Action of Nitrosyl Bromide on d-*α-Methyl*isoserine.

The *d*-amino-acid (3·6 grams) is dissolved in 3·5 grams of hydrobromic acid (sp. gr. 1·49), diluted with 3 c.c. of water, and cooled in a mixture of ice and salt. After adding 3 grams (1 c.c.) of bromine, nitric oxide is conducted through the cold solution in a fairly rapid stream for an hour. The reaction is a slow one, and proceeds without the visible evolution of nitrogen gas. A further quantity of bromine (3 grams) is now added, after which the nitric oxide is conducted into the solution rather more rapidly and with frequent shaking. The third portion of bromine is finally added, and the gas passed in until most of the free halogen disappears. When this stage is reached, the current of nitric oxide is shut off and the bulk of the residual free bromine is removed by blowing air through the dark red solution. The remainder is destroyed by the cautious addition of sulphurous acid in the cold. The almost colourless acid solution is next saturated with ammonium sulphate and extracted ten times with ether. The dried ethereal solution is evaporated under diminished pressure and the slightly brown, flaky residue recrystallised from 100 c.c. of benzene. In this way a yield amounting to more than 90 per cent. of the theoretical can readily be obtained:

0·1876 gave 0·1802 CO_2 and 0·0620 H_2O. C = 26·19; H = 3·70.
0·2277 „ 0·2334 AgBr. Br = 43·62.
$C_4H_7O_3Br$ requires C = 26·23; H = 3·83; Br = 43·71 per cent.

The optical properties were measured in approximately 10 per cent. aqueous solution:

0·3696, made up to 3·8115 (sp. gr. at 20° = 1·0446), gave in a 1-dcm. tube, α +0·75° (± 0·01), whence $[\alpha]_D^{20}$ +7·40° (± 0·20).*

d-*β-Bromo-α-methyl-lactic acid* crystallises in silky needles, which can frequently be obtained an inch long. These melt at 114° (uncorr.)—considerably higher than the racemic acid—and are readily soluble in alcohol, ether, acetone, or water. In boiling benzene the bromo-acid dissolves fairly readily, but the solution on cooling deposits almost the whole of the acid in compact, crystalline tufts.

Potassium d-*α-Methylglycidate.*

The elimination of the elements of hydrobromic acid from *d-β*-bromo-α-methyl-lactic acid can readily be effected by the action of the theoretical amount of cold alcoholic potassium hydroxide. For this purpose, 3 grams of the bromo-acid were dissolved in 5 volumes of absolute alcohol, carefully cooled in a freezing mixture, and gradually treated with a solution of 2 grams of potassium hydroxide (specially purified) in 20 c.c. of alcohol. The addition of the alkali was carried out in such a manner that the alcoholic solution always remained slightly acid, whilst care was taken that the temperature never rose above zero. By the time half the potassium hydroxide had been added, potassium bromide began to separate. After the whole of the potassium hydroxide solution had been added, the mixture was kept at 0° for several hours so that the separation of the potassium bromide might become as complete as possible. The solid deposit was now collected and washed with a little cold alcohol. As the precipitate still contained some potassium salt of the organic acid which had been carried down mechanically, it was therefore exhausted a few times with boiling absolute alcohol, yielding an extract which was worked up by itself, as described below. The potassium salt of the glycidic acid was finally precipitated from its alcoholic solutions by the addition of a large volume of ether. It was naturally contaminated with potassium bromide, which could only be removed with great difficulty. It was finally obtained practically pure by repeated recrystallisation from boiling absolute alcohol, from which it separates on cooling in silvery leaflets. The total yield of bromine-free potassium salt only amounted to 0·6 gram, or 25 per cent. of the theoretical, which is fairly satisfactory considering the method of purification.

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* A similar experiment was carried out with 2·4 grams of the racemic amino-hydroxy-acid, yielding 2·1 grams (80 per cent.) of the racemic bromo-acid melting at 102—103° (uncorr.), which is obviously identical with that described by Melikoff:

0·1754 gave 0·1782 AgBr. Br = 42·24.
$C_4H_7O_3Br$ requires Br = 43·71 per cent.

For analysis and the determination of the optical properties, the rather hygroscopic salt was dried at 95° in a vacuum over phosphoric oxide until constant in weight:

0·1856 gave 0·1158 K_2SO_4. K = 28·02.

$C_4H_5O_3K$ requires K = 27·96 per cent.

The determination of the rotatory power was carried out in approximately 10 per cent. aqueous solution:

0·3964, made up to 3·9800 (sp. gr. at 20° = 1·0460), gave in a 1-dcm. tube, α $-1·83°$ ($\pm$ 0·01), whence $[\alpha]_D^{20}$ $-17·57°$ ($\pm$ 0·20).

Potassium d-*a-methylglycidate* is sparingly soluble in cold absolute alcohol, but dissolves fairly readily in the hot solvent, and crystallises from the hot solution with the utmost readiness in mother-of-pearl leaflets, which when collected form a compact, scaly skin.

Potassium d-*a-methylglycerate.*—As stated in the introduction, the author had to content himself, for the present, with an approximate estimation of the rotatory power of this salt, which was accomplished by pouring the contents of the polarimeter tube from the above determination into a tared, stoppered flask, which was next weighed and then placed in the steam-oven for two hours, the stopper being loosely replaced so as to prevent evaporation as much as possible. When cold, the solution was diluted with water, so that it contained approximately 10 per cent. of potassium *d-a*-methylglycerate:

0·3824, made up to 3·8873 (sp. gr. at 20° = 1·0430), gave in a 1-dcm. tube α $-0·41°$ ($\pm$ 0·01), whence $[\alpha]_D^{20}$ $-4·00°$ ($\pm$ 0·20).

It is hoped later to extend these experiments by the isolation of the free *d-a*-methylglyceric acid, and also to carry out the corresponding transformations with the lævo-component.

In conclusion, the author wishes to thank Prof. Emil Fischer for the valuable advice and the kind interest he took in this work while it was being carried out in the Berlin laboratories.

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LXXII.—*A Polarimetric Method of Identifying Chitin.*

By James Colquhoun Irvine.

The numerous investigations which have been carried out during the last thirty years on the nature and distribution of chitin have been greatly hampered by the absence of any definite test for the compound. In cases where the substance can be obtained in quantity, its identification usually depends on the results of quantitative analysis supplemented by conversion into glucosamine hydrochloride. These methods are not altogether free from objection, as the analytical figures obtained are liable to show some fluctuation, and, moreover, the conversion into glucosamine hydrochloride by the process at present in use applies equally well to many nitrogenous compounds other than chitin, and is therefore inconclusive. In testing small quantities of material, even the above methods are inapplicable, and thus many natural products are classified as chitin in that they display merely the negative properties of insolubility in dilute acids and alkalis, and resistance towards the action of dilute potassium permanganate solution. Conflicting results are therefore numerous, and the question has even been raised as to whether chitin, derived from different sources, or from different organs of the same individual, is in reality a definite compound of uniform composition.

This view, however, seems to rest largely on the evidence of staining tests, which may vary greatly according to surface conditions, and thus the opinion generally prevails that chitin is a definite compound, which in many ways plays a part in invertebrate animal structure similar to that shown by cellulose in plants. Considerable support is given to this idea by the results obtained by Miss Sollas (*Proc. Roy. Soc.*, 1907, **79**, *B*, 474), who determined some physical constants of chitin obtained from various sources. It was shown that practically identical values were obtained in exact determinations of the specific gravity and also of the refractive index.

The following research was carried out in the hope that determinations of the specific rotations of chitin, together with the polarimetric study of its conversion into glucosamine hydrochloride and chitose respectively, would yield definite evidence of identity or difference in specimens of the compound obtained from widely different sources. In this connexion I take the opportunity of expressing my indebtedness to Professor W. C. McIntosh and Dr. J. R. Tosh for their kindness in providing the necessary material, and in placing at my disposal many valuable zoological specimens.

The usual method of obtaining pure chitin was followed, the final precipitation of the compound being repeated until the product was perfectly white and free from traces of ash.

Specific Rotation of Chitin in Hydrogen Chloride.

In determining the specific rotations the use of concentrated hydrochloric acid as a solvent necessitates special precautions. The metallic fittings of the polarimeter tube and its accessories were coated with a thin layer of vaseline in order to avoid corrosion by the acid, a method which did not introduce any experimental error. All the readings were taken at 20°, and the concentration used was as nearly as possible 1·75 per cent. in each case. More concentrated solutions of chitin can of course be obtained, but as the substance dissolves slowly in the acid, a considerable time must elapse in such cases before the first polarimetric readings can be taken. This is inadvisable, as the specific rotation alters appreciably on standing, and the above value for the concentration was selected as the most suitable, as a solution of this strength may be rapidly prepared. In every case the sample of chitin was finely powdered and dried at 110° until constant in weight. Although chitin doubtless dissolves in the acid owing to hydrochloride formation, the specific rotations were calculated on the weight of substance used.

The results obtained show that chitin is uniformly lævorotatory, the average value being $[\alpha]^{20}_{\mathrm{D}}$ $-14{\cdot}1^{\circ}$ in hydrochloric acid (sp. gr. 1·160).

Source of the chitin used.	Initial specific rotation.	
1. Carapace of *Homarus*	−14·7°	−13·9°
2. ,, *Cancer paguras*	13·6	
3. ,, *Limulus*	13·9	
4. ,, *Lithodes maia*	13·5	
5. Total chitin from *Crangon vulgaris*	14·6	
6. ,, *Blatta*	13·9	
7. From the beak of *Loligo*	14·1	
8. From *Flustra foliacca*	14·0	

In view of the uniformity of the specific rotations recorded above, there can be little doubt that all the specimens are identical in every respect.

Changes in Rotatory Power due to the Formation of Glucosamine Hydrochloride.

The claim for identity of the different preparations of chitin is greatly strengthened by a study of the optical changes shown by the rotation solutions on standing or on warming. Even at room temperature the specific rotations rapidly diminished, and the solution ultimately became dextrorotatory. The rate and magnitude of this characteristic "inversion" are shown in the following table:

Time in hours from start.		0.	24.	72.	720.
Chitin from *Cancer*	$[\alpha]_D^{20}$	−13·6°	−3·1°	+3·1°	+32·6°
,, *Blatta*		13·9	3·0	4·0	34·1
,, *Homarus*		14·7	3·4	4·0	32·7

The increase in dextrorotatory power continued until the constant value (calculated on the original concentration) of $[\alpha]_D^{20}$ +56° was reached in each case. This optical change, which is of course due to formation of glucosamine hydrochloride, is greatly accelerated by keeping the solution at 40—45°, the reaction being then complete in eight to ten hours. It was afterwards found that under these conditions the hydrolysis is complete and quantitative, and as no colouring matters are produced, accurate readings may be made. The polarimetric test for chitin should therefore include, not only the determination of the initial specific rotation, but also of the permanent values reached on hydrolysis. The following results show conclusively that the various preparations examined were identical substances:

Source of the chitin used.	Specific rotation after hydrolysis.	Source of the chitin used.	Specific rotation after hydrolysis.
Homarus	+55·6°	*Crangon*	56·4°
Cancer....................	56·3	*Blatta*	55·9
Limulus	56·3	*Loligo*	55·9
Lithodes	55·6	*Flustra*	56·0

Mean, 56·0°.

Action of Nitrous Acid on the Hydrolysed Solutions.

The polarimetric examination was extended by decomposing the various rotation solutions with nitrous acid and examining the activities of the resulting liquids. For this purpose 15 c.c. of each of the solutions referred to above were withdrawn, and 10 c.c. of 5 per cent. potassium nitrite solution added drop by drop. The liquid was then gently warmed until effervescence ceased and all nitrous fumes were expelled, after which it was diluted to 30 c.c. The active constituent then present in the solution is the monosaccharide chitose, the concentration of which may be calculated. The results obtained by this process were not very uniform, and, in the absence of any reliable data as to the rotatory powers of chitose, it is impossible to explain the discrepancies observed. The general result was, however, the same in every case, the specific rotations diminishing to about half the initial value :

Source of the chitin used.	$[\alpha]_D^{20}$ after hydrolysis.	$[\alpha]_D^{20}$ after conversion into chitose.
Carcinus	+56·3°	+22·7°
Homarus	55·6	22·6
Limulus	55·6	28·8
Blatta	55·9	27·4
Lithodes	56·0	25·5

Polarimetric Examination of Chitin Obtained from Different Organs of the same Individual.

The external skeleton of the edible crab was selected for experiment with the view of determining the rotatory powers of specimens of chitin derived from the various regions. The well-rotted shell was dissected after decalcification, the carapace being detached from the abdominal coating and being separately worked up. The leg cases and chelæ were also separately treated. The preparation of pure chitin from each of these regions was carried out exactly as before, and the following polarimetric results were obtained :

	Initial $[\alpha]_D^{20}$.	$[\alpha]_D^{20}$ after hydrolysis.	$[\alpha]_D^{20}$ after treatment with nitrous acid.
Carapace region	−13·6°	+55·6°	+24°
Ambulatory appendages	13·9	56·3	23°
Chelæ	13·5	55·6	26°

The results show that in the particular case studied the chitin derived from the different structures is uniform in optical properties.

Application of the Test to the Detection of Small Quantities.

In applying the polarimetric test to very small quantities of chitin, special difficulties arise, as it is almost impossible to detach the precipitated compound from the filter without fibres of the paper adhering to the product. In such a case the test may be applied by comparing the observed angles of rotation without calculating the values as specific rotations. If a_a represents the initial observed angle, and a_b, a_c the value after hydrolysis and decomposition with nitrous acid respectively, then, when the same length of observation tube is used throughout, the numerical relationship between the different values is shown in the following approximate ratio :

$$\begin{array}{ccccc} a_a & \longrightarrow & a_b & \longrightarrow & a_c \\ -1 & \longrightarrow & +4 & \longrightarrow & +\tfrac{3}{2}. \end{array}$$

This admits of the test being applied to as small a quantity as

0·1 gram. In order to obtain the maximum polarimetric reading the test specimen is dissolved in the minimum amount of hydrochloric acid necessary to fill a 1-dcm. tube, the initial angle is read, and also that observed after heating for ten hours at 45° in a stoppered flask. The experimental error is naturally large, as the readings are small, but the following figures show that nevertheless the method is fairly trustworthy:

	α_a.		α_b.		α_c.
1.	$-0·25°$	$\longrightarrow$	$+1·01°$	$\longrightarrow$	$+0·35°$
2.	0·24	,,	0·99	,,	0·34
3.	0·19	,,	0·76	,,	0·30
4.	0·12	,,	0·52	,,	0·20

In the course of the work a number of structures were examined in which the occurrence of chitin has been disputed.

Negative results were obtained in the following cases: the egg capsule of *Raia*, the "spongin" of *Halychondria* and *Chalina*, the suckers and "pen" of *Loligo*, *Alcyonium*, and the outer integument of horn.

It is hoped that the polarimetric test may be applied to establish whether the so-called "fungus cellulose" or "fungus chitin" found in *Boletus edulis* and other botanical forms is in reality identical with the chitin derived from animal sources.

Discussion of Results. Constitution of Chitin.

The polarimetric results obtained in the hydrolysis of chitin throw some light on the problem of the structure of the compound. Although molecular-weight determinations are impossible with the substance, investigators have not hesitated to speculate as to the probable complexity of the molecule, and various formulæ, framed to suit analytical results, have in turn been proposed and rejected. The original formula suggested by Ledderhose (*Zeitsch. physiol. Chem.*, 1879, **2**, 225) was apparently based on the assumption that chitin is a glucosidic compound formed by the condensation of aminoglucose and acetic acid. This view was opposed by Sundwik (*Zeitsch. physiol. Chem.*, 1881, **5**, 384), who recommended various complicated alternatives, indicating that the analytical data were best satisfied by the formula $C_{30}H_{50}O_{19}N_4$ or its multiples. He regarded chitin as a complex containing both glucose and aminoglucose residues, but questioned the presence of acyl groups. Different observers have, however, identified acetic, butyric, and formic acids among the hydrolytic products; as the reaction was in such cases carried out by boiling the solution of chitin in concentrated hydrochloric acid, it is not surprising that the two latter compounds were produced.

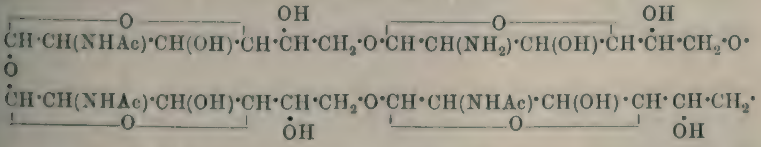
Possibly the most acceptable view is that of Fränkel and Kelly, who ascribe to chitin a molecular complexity similar to that of starch or glycogen. They also showed that chitin may be converted into acetylglucosamine, thus indicating that in the parent substance acetyl groups are united to nitrogen. Presumably in a complex of this nature the sugar residues must be directly linked, and according to this idea the hydrolytic action of hydrochloric acid consists in cleavage of the molecule, followed by removal of the acetyl groups. The simplest possible products of the hydrolysis should therefore be glucosamine hydrochloride and acetic acid. The polarimetric study of the change permits of the accurate estimation of the amount of the former compound which is produced, and the various formula suggested for chitin may thus be tested in their relationship to the results obtained.

The conclusion arrived at is that Sundvik's formula, $C_{30}H_{50}O_{19}N_4$, is the simplest one which adequately fulfils the necessary conditions, although his explanation of the mechanism of the hydrolysis is manifestly incorrect. He regards all volatile acids formed during the change as decomposition products, and applies the following equation to the reaction:

$$C_{30}H_{50}O_{19}N_4 + 7H_2O = 4C_6H_{13}O_5N + C_6H_{12}O_6.$$

This view is no longer tenable, for, as already pointed out, the hydrolysis of chitin at 45° involves no extraneous decomposition of the sugar residues, but nevertheless it was found that acetic acid was formed in quantity during the reaction. The above equation must therefore be modified.

A review of all the available data makes it possible to devise a structural formula which would at least represent a fraction of the chitin molecule. A structural formula of this kind must, in addition to satisfying analytical results, account for the following: (1) the absence of reducing properties, (2) the capacity to dissolve in hydrochloric acid, (3) the formation of a definite amount of both glucosamine hydrochloride and acetic acid on hydrolysis. These conditions are realised in the structure shown below, in which one molecule of aminoglucose is condensed with three molecules of acetylaminoglucose through the elimination of four molecules of water.



$$\begin{array}{l}\overbrace{\mathrm{CH{\cdot}CH(NHAc){\cdot}CH(OH){\cdot}CH}}^{\mathrm{O}}{\cdot}\overset{\mathrm{OH}}{\dot{\mathrm{C}}}\mathrm{H{\cdot}CH_2{\cdot}O{\cdot}}\overbrace{\mathrm{CH{\cdot}CH(NH_2){\cdot}CH(OH){\cdot}CH}}^{\mathrm{O}}{\cdot}\overset{\mathrm{OH}}{\dot{\mathrm{C}}}\mathrm{H{\cdot}CH_2{\cdot}O{\cdot}}\\ \dot{\mathrm{O}}\\ \underbrace{\dot{\mathrm{C}}\mathrm{H{\cdot}CH(NHAc){\cdot}CH(OH){\cdot}CH}}_{\mathrm{O}}{\cdot}\underset{\mathrm{OH}}{\dot{\mathrm{C}}}\mathrm{H{\cdot}CH_2{\cdot}O{\cdot}}\underbrace{\mathrm{CH{\cdot}CH(NHAc){\cdot}CH(OH){\cdot}CH}}_{\mathrm{O}}{\cdot}\underset{\mathrm{OH}}{\dot{\mathrm{C}}}\mathrm{H{\cdot}CH_2{\cdot}}\end{array}$$

The hydrolysis of such a compound would proceed according to the equation:

$$C_{30}H_{50}O_{19}N_4 + 7H_2O + 4HCl \longrightarrow 4C_6H_{13}O_5N,HCl + 3CH_3{\cdot}CO_2H,$$

so that the ratio between the weight of chitin used and that of the glucosamine hydrochloride formed is 1 : 1·1195. That this ratio holds was shown by the following exact experiment: Pure dry chitin (4·1238 grams) was dissolved in hydrochloric acid (sp. gr. 1·160) and the solution made up to 250 c.c. The rotation in a 2-dcm. tube was initially $-0·46°$ (α_D $-13·9°$), and after heating at 45° for fifteen hours was $+1·86°$. This value remained constant on continuing the hydrolysis for an additional five hours. Applying the above ratio, the concentration of the glucosamine hydrochloride then present in the solution was $c = 1·8476$, whence $[\alpha]_D^{20}$ 51·4°. A second experiment gave $+51·1°$. The rotatory power of glucosamine hydrochloride in hydrochloric acid being unknown, this value was determined, using a specimen of the compound which had been crystallised several times and gave the correct specific rotation in aqueous solution. The result obtained was:

$$c = 1·6160, l = 2, \alpha^{20} + 1·66°, [\alpha]_D^{20} + 51·3°.$$

The close agreement shows that the amount of glucosamine hydrochloride formed during hydrolysis corresponds with the given equation.

It was also possible, by evaporating the rotation solution referred to above at 50° under diminished pressure, to estimate approximately the amount of acetic acid formed during the reaction. During this treatment, judging from the fact that the liquid remained practically colourless, no secondary decomposition took place. The acetic acid present in the distillate was estimated according to the method adopted by Ledderhose. The result indicated the presence of 0·5598 gram of acetic acid, a value which is about two-thirds of the calculated amount. Taking into consideration the fact that extreme accuracy cannot be claimed for an estimation which involves distillation under diminished pressure, the result may be taken as an indication that more than two molecular proportions of acetic acid are produced in the hydrolysis. In order to confirm the absence of butyric acid, a portion of the acid distillate was converted into the barium salt; the product on analysis gave Ba = 53·1, whereas theory requires Ba = 53·8 per cent. The combined results are therefore in agreement with the idea that the formula for chitin is $(C_{30}H_{50}O_{19}N_4)_n$, containing acetylaminoglucose and aminoglucose residues in the proportion of three to one.

The general expenses of the above investigation were defrayed by a research grant from the Carnegie Trust, for which I desire to express my thanks.

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LXXIII.—*The Alkyl Compounds of Platinum.*

By William Jackson Pope and Stanley John Peachey.

Some years ago we observed that many inorganic chlorides, bromides, and iodides react vigorously with the Grignard reagent, and showed that the alkyl compounds of tin may be conveniently prepared by the action of the magnesium alkyl chlorides, bromides, or iodides on stannic chloride (Proc., 1903, **19**, 290). Since that time Pfeiffer and his co-workers have applied the reaction to the preparation of a number of other organo-metallic compounds, and Kipping has shown that the alkyl silicon compounds can in many cases be readily prepared by its aid. The Grignard reagent not only furnishes a convenient means for preparing organo-metallic compounds of the types which had been previously discovered, principally by E. Frankland, with the aid of the zinc alkyl compounds, but Pope and Gibson have shown (Trans., 1907, **91**, 2061) that the gold alkyl compounds, which were previously unknown, can be prepared by the action of magnesium alkyl iodides on auric bromide. Frankland has noted (*Quart. Journ. Chem. Soc.*, 1861, **13**, 188) that, although the zinc alkyl compounds act violently on halogen compounds of platinum, the organic group does not unite with the metal. In the present paper we describe the preparation and properties of a new series of organo-metallic compounds, namely, those of platinum, which are obtained by the action of magnesium methyl iodide on platinic chloride.

By aid of the reaction just mentioned, we have succeeded in obtaining *trimethylplatinic iodide*, $(CH_3)_3PtI$, which proves to be a salt-like substance derived from a very feebly basic hydroxide, *trimethylplatinic hydroxide*, $(CH_3)_3Pt\cdot OH$. The examination of the latter substance and its salts indicates that the quadrivalent platinum atom resembles the quinquevalent nitrogen atom, in that it appears impossible to attach four alkyl groups to the former just as it is impossible to obtain compounds in which five basic groups are attached to the same nitrogen atom. The new substances now described are further of importance in that they are the first representatives to be prepared of the alkyl derivatives of the nine metals composing group VIII of the periodic classification.

Trimethylplatinic Iodide, $(CH_3)_3PtI$.

The successful preparation of trimethylplatinic iodide requires attention to a number of details, and it is consequently desirable to describe the necessary precautions at some length. Chloroplatinic acid, contained in a distilling flask, is heated at 200° in a metal-bath under a low atmospheric pressure, the water and hydrogen chloride evolved being absorbed by suction through a Woulff's bottle containing solid potassium hydroxide; after some hours' heating, decomposition comes to an end, and nearly pure platinic chloride remains in the distilling flask. This material is treated with anhydrous ether in sufficient quantity to dissolve part of it and to convert the remainder into a dark red syrup; the solution and syrup are then slowly run into a solution of magnesium methyl iodide, the mixture being constantly cooled and shaken. The magnesium methyl iodide solution used is prepared with the aid of the minimum quantity of ether, and is afterwards diluted with five volumes of anhydrous benzene; a considerable excess of the magnesium methyl iodide is used, about twice as much as is indicated by the following equation:

$$PtCl_4 + 3CH_3{\cdot}MgI = (CH_3)_3PtI + 2MgCl_2 + MgI_2.$$

The addition of the platinic chloride solution to the Grignard reagent leads to a vigorous reaction accompanied by considerable evolution of heat. After standing for an hour, the mixture is poured into ice-water and the benzene solution separated, the aqueous solution being subsequently extracted several times with benzene. After washing with water, the benzene extracts are distilled from the water-bath under diminished pressure, when a heavy sandy powder of a brownish-yellow colour remains behind. This dissolves readily in boiling benzene, and, after filtration, the solution on rapid cooling deposits trimethylplatinic iodide as a bright yellow, crystalline powder.

The analysis of the substance presents some difficulties, owing to a tendency to explosive decomposition on heating. The platinum may be determined by treating a weighed quantity with solid iodine and a few drops of chloroform in a porcelain crucible and very slowly heating to redness. The iodine is determined by slowly heating with lime and titrating in the usual way with silver nitrate and thiocyanate solutions:

0·1500 gave 0·0795 Pt. Pt = 53·00.
0·2308 ,, 0·0791 I. I = 34·27.
C_3H_9IPt requires Pt = 53·10; I = 34·61 per cent.

Trimethylplatinic iodide dissolves freely in hot benzene or chloroform and crystallises well from either solvent. On slow evaporation of its solution in benzene it separates in square, doubly refracting plates of an amber-yellow colour, which rapidly become opaque owing to loss of solvent of crystallisation. It is readily soluble in cold ethyl bromide or methyl iodide, and from solutions in the former is deposited in hexagonal plates which apparently belong to the cubic system. It is insoluble in water and very sparingly soluble in ether, alcohol, acetone, or light petroleum. The substance is not attacked in the cold by bromine or iodine, nor by concentrated acids or alkalis; alkali sulphides cause no darkening in colour. When heated with concentrated nitric acid it slowly dissolves, with elimination of iodine, and on evaporating the solution a white residue remains which explodes on further heating, giving a mixture of carbon and platinum.

On heating with concentrated sulphuric acid, the substance slowly dissolves, leaving a black residue which probably consists of platinum; part of the iodine is expelled by this treatment and the remainder is given off on evaporating and heating, a residue of platinum remaining. When heated alone, the compound decomposes with a slight explosion, leaving a sooty residue of carbon and platinum; when slowly heated in a melting-point tube a gradual decomposition occurs and appears to be complete below 250°. On heating in a flame, the substance catches fire and burns with a smoky, lurid flame, leaving a residue of platinum.

Diamminotrimethylplatinic Iodide, $(CH_3)_3PtI(NH_3)_2$.

The difficulty with which ammonia acts on trimethylplatinic iodide led at first to the view that no combination could be induced between these two substances; more careful investigation showed, however, that the iodide combines with two molecular equivalents of ammonia in accordance with Werner's classification. On heating trimethylplatinic iodide with a mixture of benzene, alcohol, and concentrated ammonia on the water-bath and evaporating to dryness, white, crystalline scales are deposited. The substance thus produced is but slightly soluble in water, moderately so in benzene or ether, and dissolves very readily in alcohol, ethyl acetate, or acetone; it is practically insoluble in chloroform or light petroleum, and yields free ammonia on heating with potassium hydroxide:

0·2291 gave 0·1106 Pt. Pt = 48·27.

$C_3H_{15}N_2IPt$ requires Pt = 48·58 per cent.

It is noteworthy that whilst the diauric halogen compound forms a monoammino-derivative, $(C_2H_5)_2AuBr(NH_3)$ (Trans., 1907, **91**, 2065), the corresponding trialkylplatinic compound yields a diammino-derivative, $(CH_3)_3PtI(NH_3)_2$, in accordance with Werner's theory.

Trimethylplatinic Hydroxide, $(CH_3)_3Pt{\cdot}OH$.

This substance is prepared by boiling trimethylplatinic iodide in moist acetone solution with freshly precipitated silver hydroxide; the conversion occurs but slowly under these conditions, and is greatly expedited by addition of benzene, which dissolves the iodide and hydroxide and forms a separate layer of liquid floating on the acetone solution. After filtration and washing with water, the benzene solution is evaporated, when the hydroxide separates in almost colourless, transparent crystal plates, which rapidly become opaque in the air. The crude trimethylplatinic hydroxide obtained in this way is purified by crystallisation from benzene; it is deposited in massive square tablets, which are colourless and transparent, but become opaque on washing with light petroleum owing to loss of solvent. The crystals are doubly refracting, and show straight extinction and a perfect cleavage parallel to their longer edges; they contain benzene of crystallisation, but the proportion of this could not be ascertained owing to the rapidity with which efflorescence occurs on exposure to the air. On heating, the substance burns explosively, leaving a sooty residue of carbon and platium; it was analysed by gently incinerating with hydriodic acid, after heating at 100° until all the benzene had been driven off:

0·1666 gave 0·1261 Pt. $Pt = 75·69$.

$C_3H_{10}OPt$ requires $Pt = 75·83$ per cent.

Trimethylplatinic hydroxide is fairly soluble in ether, alcohol, acetone, ethyl acetate, chloroform, or benzene, and crystallises from the last three solvents named with solvent of crystallisation, which is quickly lost in the air. From alcohol or chloroform solutions it separates in solvent-free and nearly colourless crystals; these are transparent, highly refractive, rhombic dodecahedra belonging to the cubic system. The substance is insoluble in water, alkalis, or light petroleum; it is not attacked in the cold by mineral acids, but dissolves on warming with nitric acid. Concentrated sulphuric acid partly decomposes the hydroxide.

Trimethylplatinic Sulphate, $(Me_3Pt)_2SO_4,2H_2O$.

Dilute sulphuric acid has little action on trimethylplatinic hydroxide, but the sulphate is conveniently prepared by boiling equivalent quantities of trimethylplatinic iodide and silver sulphate with a mixture of moist acetone and benzene under a reflux condenser for several hours. After action has ceased, the solution is filtered and evaporated, when *trimethylplatinic sulphate* separates in small, colourless, rectangular plates, which are transparent and show straight extinction.

The salt is readily soluble in water, alcohol, or acetone, but practically insoluble in benzene, light petroleum, ether, or chloroform. It is most conveniently crystallised from water, but is difficult to purify owing to its ready solubility; the substance thus obtained contains water of crystallisation, which it apparently retains at 100°. The platinum was determined in material dried at 100° by slowly incinerating after addition of iodine and chloroform ; the sulphur was estimated by precipitation with barium nitrate solution :

0·2560 gave 0·1626 Pt. Pt = 63·51.
0·3612 „ 0·1333 $BaSO_4$. $SO_4 = 15{\cdot}18$.
$C_6H_{18}O_4SPt_2,2H_2O$ requires $Pt = 63{\cdot}67$; $SO_4 = 15{\cdot}70$ per cent.

It was not found possible to make a combustion of the substance owing to its explosive decomposition on heating alone, and as it decomposes when heated sufficiently to drive off the water of crystallisation, a direct determination of the latter was not attempted.

Trimethylplatinic Nitrate.

Trimethylplatinic hydroxide dissolves fairly readily when warmed with concentrated nitric acid, or when boiled for some time with the diluted acid, forming a nitrate which is very soluble and difficult to crystallise, especially from the acid solution. The crystalline salt is more easily prepared by treating an aqueous solution of trimethylplatinic sulphate with an equivalent amount of barium nitrate, filtering from barium sulphate, and evaporating. It separates from the pure aqueous solution in colourless, crystalline plates, which are so markedly deliquescent that their analysis was not attempted. The crystals are thin, flat plates with replaced ends ; the large face is perpendicular to the acute bisectrix of a fairly large optic axial angle, the extinction is straight, and the double refraction is negative in sign.

Owing to their ready solubility in water, trimethylplatinic sulphate and nitrate form convenient sources from which to derive a number of more sparingly soluble salts of the new base.

Trimethylplatinic Chloride, $(CH_3)_3PtCl$.

Trimethylplatinic chloride is easily prepared by precipitating an aqueous solution of the nitrate or sulphate with potassium chloride or by dissolving the hydroxide in alcohol and evaporating to dryness after addition of hydrochloric acid. It is practically insoluble in water, dissolves very sparingly in acetone, alcohol, or ethyl acetate, and is moderately soluble in benzene or chloroform, although distinctly less so than is the iodide. The substance crystallises from chloroform solutions in colourless, rhombic dodecahedra, which belong to the cubic system and contain no solvent of crystallisation. The following analysis was made by gently heating the substance in presence of iodine and chloroform and subsequently igniting strongly :

0·1840 gave 0·1300 Pt. Pt = 70·65.

C_3H_9ClPt requires Pt = 70·75 per cent.

Trimethylplatinic Cyanide, $(CH_3)_3Pt\cdot CN$.

On adding potassium cyanide to a solution of trimethylplatinic nitrate or sulphate, a white, flocculent precipitate is thrown down which is partly soluble in excess of the precipitant; the substance is insoluble in water, and too sparingly soluble in organic solvents to allow of its ready purification. It was not obtained in crystalline form, and was consequently not analysed. When boiled with sodium hydroxide, ammonia is evolved, but no hydrolytic product of the nature of a carboxylic acid could be isolated from the small quantity available for investigation.

Potassium Trimethylplatinic Platinocyanide, $K(Me_3Pt)Pt(CN)_4$.

The addition of potassium platinocyanide to an aqueous solution of trimethylplatinic nitrate causes the deposition of a slimy, yellow precipitate, which is very difficult to filter and wash. It is insoluble in water and the usual organic solvents with the exception of acetone and alcohol, in which it dissolves freely; on evaporation of its solutions in the latter solvents, it remains as an amorphous, resinous film of a greenish-yellow colour. On igniting a known weight of this substance with iodine, white fumes of potassium cyanide were evolved at a red-heat; after prolonged ignition over the blow-pipe, the residue was weighed as platinum:

0·1730 gave 0·1168 Pt. Pt = 67·51.

$C_7H_9N_4KPt_2$ requires Pt = 67·42 per cent.

It thus appears that the precipitate formed by potassium platinocyanide in a solution of trimethylplatinic nitrate consists of a *potassium trimethylplatinic platinocyanide* of the composition

$$K_2Pt(CN)_4,(Me_3Pt)_2Pt(CN)_4.$$

We desire to express our thanks to Mr. George Matthey, F.R.S., for generously allowing us the use of the platinum required for this work.

The Chemical Laboratories, University of Cambridge.
Municipal School of Technology, University of Manchester.

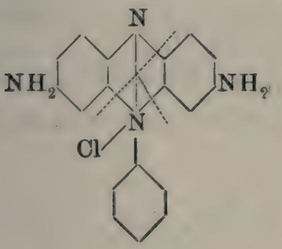
LXXIV.—*Studies in the Azine Series. Part I. The Constitution of Safranine.*

By JOHN THEODORE HEWITT, SIDNEY HERBERT NEWMAN, and THOMAS FIELD WINMILL.

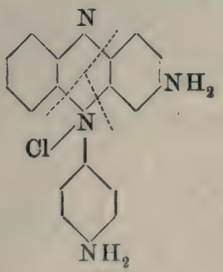
THE dyestuffs known as safranines, obtained by the oxidation of two molecules of a monoamine together with one molecule of a paradiamine, have occupied the attention of many chemists for the greater part of half a century, and it is surprising when one considers the enormous amount of experimental detail which has been accumulated, that any doubt should yet exist, not only with regard to the quinonoid constitution, but even as to the orientation of the amino-groups in this class of compounds. Even after the composition of the salts of the safranines had been definitely settled by analysis and the formation of the so-called phenosafranine hydrochloride by the oxidation of neutral salts of aniline and *p*-phenylenediamine had been shown to be in accordance with the equation:

$$2C_6H_5{\cdot}NH_2 + C_6H_4(NH_2)_2 + HCl + 4O = 4H_2O + C_{18}H_{15}N_4Cl,$$

it was not recognised for some years that these compounds were phenylphenazonium derivatives, and even then the position of the amino-groups remained in doubt, for it is evident that a diaminophenylphenazonium chloride, $C_{18}H_{15}N_4Cl$, might consistently with its derivation from one molecule of *p*-phenylenediamine and two molecules of aniline be constituted in either of the two ways shown in the formulæ (I) and (II).*



(I.)



(II.)

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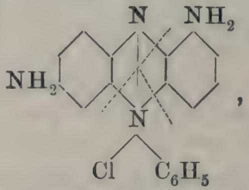
* We do not intend in this communication to go into the question of the arrangement of the linkings in the safranine and phenylphenazonium nuclei. Assuming, as we shall presently show is correct, that phenosafranine is a symmetrical compound, it may be formulated with a paraquinonoid (O. Fischer and E. Hepp, *Ber.*, 1897, **30**, 396), orthoquinonoid (compare Kehrmann, *Ber.*, 1896, **29**,

Considerable discussion arose as to the relative probabilities of these two orientations, formula (I) being advocated by Bernthsen (*Ber.*, 1886, **19**, 2690) and formula (II) by Witt (*Ber.*, 1886, **19**, 3121). The fact that a safranine can be obtained by oxidising molecular proportions of a para-diamine in which only one amino-group is primary, together with a primary monoamine in which the para-position need not be free and a substituted monoamine which must have a free para position, will agree equally well with both formulæ, although it effectually precludes the structure :



which would allow the employment of secondary and tertiary derivatives of *p*-toluidine.

Nietzki (*Ber.*, 1883, **16**, 470 ; 1886, **19**, 3021), who upheld the asymmetric formula of Witt, concluded that different diethylphenosafranines were obtained according to whether one oxidised one molecule of *p*-aminodiethylaniline together with two molecules of aniline, or employed one molecule each of aniline and its diethyl derivative with unsubstituted *p*-phenylenediamine. Nietzki's results were afterwards corrected by Körner and Schraube (*Chem. Zeit.*, 1893, **17**, 305), who showed that identical products resulted if the second molecule of monamine were only added after completion of indamine formation. In fact, Nietzki himself subsequently furnished confirmatory evidence by the synthesis of monophenylphenosafranine from (*a*) equal molecules of *m*- and *p*-aminodiphenylamine and (*b*) equivalents of diphenyl-*m*-phenylenediamine and *p*-phenylenediamine, the products being identical (*Ber.*, 1896, **29**, 1442).

The evidence, it will be noted, for the symmetrical structure of

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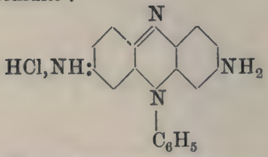
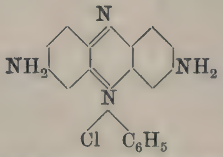
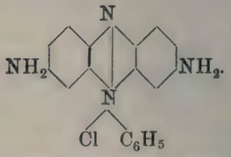
2316 ; Nietzki, *ibid.*, **29**, 2771), or cross-linked structure, as shown in the following formulæ :

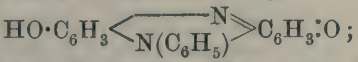






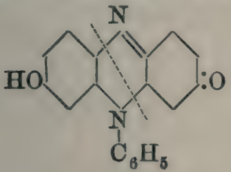
Whilst we hope to examine this question in the near future, we are at present only concerned with the question of orientation, and in using the somewhat indefinite formulæ (I) and (II), and giving to hydroxyaposafranone (safranol) a paraquinonoid structure, instead of writing it as an internal orthoquinonoid anhydride, we do so without prejudice.

phenosafranine is indirect, resting on the synthesis of substituted derivatives. But Nietzki and Otto had obtained by removal of the amino-groups from safranine a compound of the formula $C_{18}H_{12}O_2N_2$, the structure of which is that of a hydroxyaposafranone (safranol: Nietzki and Otto, *Ber.*, 1888, **21**, 1593),

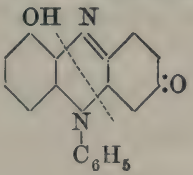


$$HO\cdot C_6H_3<\overset{N}{\underset{N(C_6H_5)}{}}>C_6H_3{:}O;$$

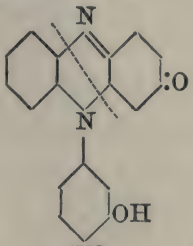
and the synthesis by G. F. Jaubert (*Ber.*, 1895, **28**, 273) of an apparently identical compound from nitrosophenol and *m*-hydroxydiphenylamine would appear to leave no doubt of the constitution of this substance and also that of phenosafranine, for the production of a quinonoid compound can only take place in such a way as to furnish a substance having one of the three following constitutions:



(I.)



(II.)



(III.)

It is on a priori grounds probable that a substance having constitution (I) would be produced, whilst if the substance is really identical with Nietzki's safranol, no other formula is possible, for although structure (I) agrees with Bernthsen's formula for phenosafranine, constitutions (II) and (III) cannot be derived from either of the formulæ which have been assigned to the diamino-compound. Unfortunately, no direct comparison was made, and the definite proof of Bernthsen's formulation of phenosafranine remained incomplete.

Meanwhile, P. Barbier entered the field and gradually came to the conclusion that phenosafranine is a mixture of two isomerides, the major portion of the colouring matter consisting of a substance having the structure ascribed by Witt to phenosafranine, whilst only a small portion corresponded with the symmetrical formula. The results of these researches were collected and published by Barbier and Sisley in a long paper (*Ann. Chim. Phys.*, 1908, [viii], **13**, 96), in which not only was the separation of the isomerides and many of their physical properties described (solubility, electrical conductivity, and absorption spectra of salts), but the synthesis of an apparently undoubted unsymmetrical phenosafranine was also effected.

For the synthesis of the unsymmetrical phenosafranine, Barbier and Sisley added a solution of potassium dichromate to a neutral solution of equimolecular quantities of 2 : 4′-diaminodiphenylamine and aniline, subsequently boiling the solution; the product they obtained showed after seven or eight recrystallisations the colour reactions of phenosafranine. (Red aqueous solution, the colour passing first into blue and then green by addition of an excess of sulphuric acid.)

The apparent definiteness of the results obtained by Barbier and Sisley led one of the present authors at first to form the opinion that in the particular case of the simplest safranine the condensation follows an abnormal course, but further reflection made it appear worth while to examine the subject further and the results obtained are now recorded.

Briefly stated the results are as follows: The safranol obtained from safranine by Nietzki's method is identical with that synthesised by Jaubert, for both products furnish acetyl derivatives of identical melting point which showed no depression on mixing the specimens. Further, the supposed synthesis of phenosafranine from 2 : 4′-diaminodiphenylamine and aniline is incorrect, for the former merely yields aminophenazine, whether aniline is present or not.

Preparation of Hydroxyaposafranone.—Jaubert's method of heating an aqueous solution of nitrosophenol, *m*-hydroxydiphenylamine, and sodium hydroxide (*Ber.*, 1895, **28**, 273) was closely followed, except in so far as the sodium salt of nitrosophenol which he employed was replaced by the equivalent amounts of the free phenol and sodium hydroxide. The only analysis given by Jaubert is a single estimation of sodium in the sodium derivative. So as to confirm the purity of the product (Jaubert's figures not being in close agreement with the theory), we decomposed some of the recrystallised sodium salt by acid and prepared derivatives. The free hydroxyaposafranone, although apparently crystalline, furnished extremely badly agreeing results on analysis; various specimens gave $C = 73{\cdot}3—73{\cdot}6$, $H = 4{\cdot}6$, whilst $C_{18}H_{12}O_2N_2$ requires $C = 75{\cdot}0$, $H = 4{\cdot}2$ per cent. It thus appeared very doubtful whether the substance really possessed the formula that had been assigned to it. Both Nietzki and Jaubert found that their products were nearly insoluble in the usual solvents, although readily dissolved by alkalis, and as the substance does not melt on heating, control of purity is difficult.

Eventually the following method of purification was found to give satisfactory results. Five grams of hydroxyaposafranone, as obtained by decomposition of its crystallised sodium salt, were dissolved to 100 grams of phenol at 150°, the solution filtered, and while still warm mixed with 100 c.c. of alcohol. The crystals thus obtained were collected and well washed with alcohol, dissolved in 50 grams of phenol, the solution cooled, treated with 20 c.c. of alcohol, and left overnight. The crystals after collection and washing with alcohol were well boiled with water, collected, washed, and dried at 120°:

0·2000 gave 0·5497 CO_2 and 0·0767 H_2O. C = 75·0; H = 4·3.
$C_{18}H_{12}O_2N_2$ requires C = 75·0; H = 4·2 per cent.

That the result is not due to an accidental balancing of impurities was shown by a separate experiment, in which 1 gram of hydroxyaposafranone (prepared from its sodium salt) was dissolved in 10 grams of phenol, and, while hot, treated with 20 c.c. of alcohol. A crop (*A*) of crystals was obtained, which was washed and dried in the usual manner. The phenolic-alcoholic filtrate furnished a second crop (*B*) by treatment with alcohol and boiling water; this crop was also washed and dried at 110—115°. Both crops had the appearance of pure substances, crystallising in leaflets with a splendid metallic reflex, but whilst crop *A* gave C = 74·42, H = 4·35 on analysis, crop *B* gave C = 72·64, H = 4·40 per cent. It is thus evident that the unknown impurity accumulates in the mother liquor. The properties of hydroxyaposafranone are those recorded by Nietzki and Otto, Jaubert, and Fischer and Hepp.

Acetyl Derivative.—Hydroxyaposafranone, prepared by Jaubert's method, was boiled for two hours with four times its weight of acetic anhydride. On pouring the product into hot water, the acetyl derivative separated immediately in a beautifully crystalline condition, as stated by Fischer and Hepp (*Ber.*, 1907, **30**, 401):

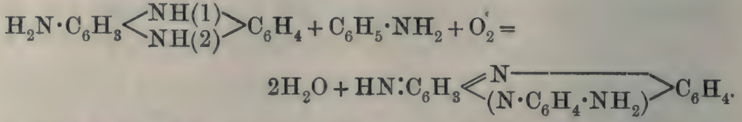
0·2005 gave 15·0 c.c. N_2 at 19° and 760 mm. N = 8·6.
$C_{20}H_{14}O_3N_2$ requires N = 8·5 per cent.

The specimen melted at 271° (uncorr., fairly rapid heating) and decomposed vigorously. Fischer and Hepp give 265—268° for their product, which was obtained evidently from hydroxyaposafranone prepared from safranine.

Hydroxyaposafranone was also prepared by the method given by Nietzki and Otto, and acetylated; the observed melting point in this case was 271° (uncorr.), and no depression was observed on mixing the specimens.

The slight difference in the melting point from that given by Fischer and Hepp is to be ascribed to difference in rate of heating. If the bath is warmed very rapidly, decomposition is avoided, and in this way results as high as 275° have been recorded.

It remains to examine Barbier and Sisley's synthesis of phenosafranine from 2:4′-diaminodiphenylamine and aniline. These authors (*loc. cit.*, pp. 101, 102) assume that when *p*-phenylenediamine is oxidised together with aniline, one molecule of each component produce together an aminodihydrophenazine, which then undergoes further condensation with the other molecule of aniline in the following manner :

(4) 

$$H_2N\cdot C_6H_3{<}\begin{matrix}NH(1)\\NH(2)\end{matrix}{>}C_6H_4 + C_6H_5\cdot NH_2 + O_2 = 2H_2O + HN{:}C_6H_3{<}\begin{matrix}N\text{———————}\\(N\cdot C_6H_4\cdot NH_2)\end{matrix}{>}C_6H_4.$$

It is most unlikely that such an aminodihydrophenazine would do otherwise than oxidise immediately to the aminophenazine melting at 265°, described by O. Fischer and E. Hepp (*Ber.*, 1889, **22**, 357; 1896, **29**, 1875), and further examined by Nietzki and O. Baur (*Ber.*, 1895, **28**, 2976, 2979). The solution of 2 : 4′-diaminodiphenylamine used by Barbier and Sisley was prepared by the reduction of 2-nitro-4′-aminodiphenylamine, which had in turn been obtained by the condensation of *o*-chloronitrobenzene with *p*-phenylenediamine. An admixture of the 4 : 4′-derivative with the 2 : 4′-compound in such a preparation is not merely possible, but even probable. *o*-Chloronitrobenzene, if prepared from chlorobenzene by nitration, is most difficult to separate from the para-isomeride, and even supposing that a pure specimen obtained from *o*-nitroaniline were employed, the elimination of a molecule of ammonia from two molecules of *p*-phenylenediamine with production of 4 : 4′-diaminodiphenylamine is not unlikely at 200°.

In order to repeat the synthesis effected by Barbier and Sisley with materials of undeniable purity, the solutions of the 2 : 4′- and 4 : 4′-diaminodiphenylamines were prepared by reduction of the corresponding dinitro-compounds. The latter substances were first prepared by Witt by the nitration of crude nitrosodiphenylamine (*Ber.*, 1878, **11**, 758), and subsequently examined by Lellmann (*Ber.*, 1882, **15**, 828), the constitution of the 2 : 4′-derivative being finally settled by Nietzki and Baur (*loc. cit.*). Since any possible isomeric admixture had to be rigidly guarded against, the necessary dinitro-compounds were prepared by the condensation of *o*- and *p*-bromonitrobenzene respectively with *p*-nitroaniline in the presence of potassium carbonate, cuprous iodide being used as catalyst (Irma Goldberg, D.R.-P. 185663).

2 : 4′-*Dinitrodiphenylamine*, obtained in this way from *p*-nitroaniline and *o*-bromonitrobenzene (prepared from *o*-nitroaniline by the Sandmeyer reaction) by heating at 195—200° for about one hour, melted, after two crystallisations from glacial acetic acid, at 218° (uncorr.); Witt gives 211·5° and Lellmann 219—220°. The yield of the crude product was nearly theoretical:

0·1152 gave 16·3 c.c. N_2 at 17° and 754 mm. N = 16·3.

$C_{12}H_9O_4N_3$ requires N = 16·2 per cent.

4 : 4′-*Dinitrodiphenylamine* was prepared by heating the necessary materials for one hour at 210—220°; after repeated recrystallisation from glacial acetic acid the substance melted at 213° (uncorr.); Witt gives 214° and Lellmann 216°:

0·1164 gave 16·3 c.c. N_2 at 17° and 754 mm. N = 16·1.

$C_{12}H_9O_4N_3$ requires N = 16·2 per cent.

Oxidation of 4 : 4′-*Diaminodiphenylamine together with Aniline.*

Two grams of 4 : 4′-dinitrodiphenylamine and 30 c.c. of glacial acetic acid were heated to about 100°, and zinc dust added until all colour was discharged. After removal of excess of zinc dust, the solution was diluted to about 100 c.c. with water, and in succession 0·76 gram of aniline and 2·3 grams of potassium dichromate dissolved in 25 c.c. of water were added. Successive indamine and safranine formation were observed; the colouring matter was isolated, and showed the colour reactions of phenosafranine. For purposes of control the platinichloride was prepared and analysed:

0·1340 gave 0·0266 Pt. Pt = 19·8.

$(C_{18}H_{15}N_4)_2PtCl_6$ requires Pt = 19·8 per cent.

Oxidation of 2 : 4′-*diaminodiphenylamine together with Aniline.*

Four grams of 2 : 4′-dinitrodiphenylamine dissolved in 80 c.c. of glacial acetic acid were reduced with zinc dust, the solution diluted, and aniline (1·5 gram) and potassium dichromate (4·6 grams) successively added. No indamine formation could be observed, and an experiment in which the aniline was omitted followed exactly the same course as when this base was present. The colouring matter produced was dissolved as far as possible, salted out, the hydrochloride decomposed by ammonia (the substance is undoubtedly a weak base and quite distinct from a powerfully basic safranine), and crystallised, first from a mixture of benzene and alcohol, then from aqueous alcohol. The resulting dark brown substance was free from halogen and proved to be aminophenazine, for it melted at 265—268° (uncorr.); it sublimed easily, and the nitrogen estimation is quite incompatible with any other substance which could be formed in the reaction:

0·1017 gave 18·0 c.c. N_2 at 17° and 773 mm. N = 21·2.

$C_{12}H_9N_3$ requires N = 21·5 per cent.

It should be noted that in working up the product of the oxidation, each extract as well as the residue was treated with concentrated hydrochloric acid, but in no case could the blue reaction due to an acid salt of a safranine be detected.

In conclusion, we wish to tender our best thanks to Mr. Zilz of the Badische Co., who very kindly procured for us a fine specimen of phenosafranine; and to the Government Grant Committee of the Royal Society for a grant by which a great part of the expense of the investigation has been defrayed.

EAST LONDON COLLEGE.

LXXV.—*Condensations of Cyanohydrins. Part I. Condensation Products from Anisaldehydecyanohydrin and Cinnamaldehydecyanohydrin.*

By HAMILTON McCOMBIE and ETHEL PARRY, M.Sc. (Priestley Research Scholar of the University of Birmingham).

BY saturating a solution of benzaldehydecyanohydrin in absolute ether with hydrogen chloride, Minovici (*Ber.*, 1899, **32**, 2206) obtained a yellow compound of the formula $C_{16}H_{12}ON_2$:

$$2C_6H_5{\cdot}CH(OH){\cdot}CN = C_{16}H_{12}ON_2 + H_2O.$$

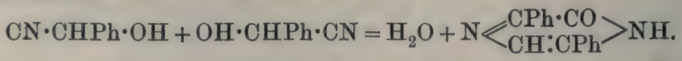
He found that the substance was not hydrolysed by heating either with potassium hydroxide or with hydrochloric acid, and suggested that it might have the constitution

$$C_6H_5{\cdot}CH(CN){\cdot}C(OH)(CN){\cdot}C_6H_5,$$

but stated that the reactions of the compound were not compatible with this formula.

Japp and Knox (Trans., 1905 **87**, 701) showed that this compound was identical with a substance which Japp and Miller (Trans., 1887, **51**, 29) obtained, along with other products, by dissolving benzil in alcohol, adding a considerable excess of anhydrous hydrocyanic acid, and saturating the liquid with hydrogen chloride.

The reactions of the compound led Japp and Knox to regard it as 3-keto-2 : 5-diphenyl-3 : 4-dihydro-1 : 4-diazine, formed according to the scheme:



$$CN{\cdot}CHPh{\cdot}OH + OH{\cdot}CHPh{\cdot}CN = H_2O + N\lessdot\begin{matrix}CPh{\cdot}CO\\CH{:}CPh\end{matrix}\gtrdot NH.$$

In the same paper, Minovici describes the effect of saturating a solution of anisaldehydecyanohydrin in absolute ether with hydrogen chloride. By this means he obtained a compound melting at 145°, and his analyses agreed with the formula $C_{17}H_{15}O_3N$. It is seen that this compound differs from the corresponding benzaldehydecyanohydrin derivative in that it contains only one atom of nitrogen, Further, it cannot be hydrolysed by heating either with potassium hydroxide or with hydrochloric acid. Minovici suggested as a possible constitution for this compound:

$$CH_3\cdot O\cdot C_6H_4\cdot CH(CN)\cdot CO\cdot C_6H_4\cdot O\cdot CH_3,$$

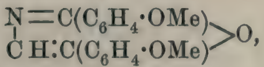
but he admitted that the properties are scarcely in harmony with such a formula.

This striking difference between the behaviours of benzaldehydecyanohydrin and anisaldehydecyanohydrin when subjected to the action of dehydrating agents led us to investigate the matter more fully.

We found that, unless the hydrogen chloride was absolutely dry, *p*-methoxymandelamide, $CH_3\cdot O\cdot C_6H_4\cdot CH(OH)\cdot CO\cdot NH_2$, m. p. 161°, was formed.

In the experiment, as conducted by Minovici, no particular precautions were taken to purify the cyanohydrin from any admixed aldehyde. On repeating his experiment we obtained a small amount of a white solid melting at 145°. In order to obtain a better yield, pure anisaldehydecyanohydrin was dissolved in absolute ether and the solution saturated with hydrogen chloride. Under these conditions, a mixture of two substances was obtained. About one quarter of the mixture consisted of a yellow, crystalline substance, which contained no chlorine and melted at 156°. The rest of the mixture consisted of a substance which melted at 223° and contained chlorine. No trace of the white solid melting at 145° was now found.

At first the compound melting at 156° was considered to be merely a purer form of the compound which Minovici described as being formed in this reaction. This appeared improbable, however, seeing that we were now dealing with a yellow substance crystallising in needles, whereas Minovici describes his substance as crystallising in white, flat leaflets. Some of the compound melting at 145° was obtained by using impure anisaldehydecyanohydrin, and it was proved to be 2:5-di-*p*-methoxydiphenyloxazole. A determination of the melting point of a mixture of the two substances proved conclusively that they were not identical. Curiously enough, 2:5-di-*p*-methoxydiphenyloxazole,



$$\begin{array}{l} N{=}C(C_6H_4\cdot OMe) \\ \mid \\ CH{:}C(C_6H_4\cdot OMe) \end{array}\!\!>O,$$

was originally described by Minovici himself (*Ber.*, 1896, **29**, 2100).

Analyses of this substance (m. p. 156°) agree with the molecular formula $C_{16}H_{14}O_3N$. We intend to investigate its structure more fully.

The major part of the solid precipitated when dry hydrogen chloride acts on anisaldehydecyanohydrin consisted of a solid melting at 223°. This substance proved to be a hydrochloride, which, on heating, lost hydrogen chloride and yielded the free base; this was found to be 3-*keto*-2 : 5-*di*-p-*methoxydiphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, $N\left\langle\begin{matrix}C(C_6H_4\cdot OMe)\cdot CO\\ CH{:}C(C_6H_4\cdot OMe)\end{matrix}\right\rangle NH$; in other words, the compound formed is the dimethoxy-derivative of the base which Minovici obtained on dehydrating benzaldehydecyanohydrin. It yields a *picrate*, which crystallises from glacial acetic acid with two molecules of the solvent.

On subjecting cinnamaldehydecyanohydrin to the action of dry hydrogen chloride, 3-*keto*-2 : 5-*distyryl*-3 : 4-*dihydro*-1 : 4-*diazine* resulted, the condensation taking place in exactly the same way as was the case with benzaldehydecyanohydrin.

EXPERIMENTAL.

Preparation of Anisaldehydecyanohydrin.

Originally, anisaldehydecyanohydrin was prepared according to the method described by Knorr (*Ber.*, 1904, **37**, 3173). As, however, it was particularly desirable that the cyanohydrin should be pure, and especially that it should be entirely free from any admixed aldehyde, the process was considerably modified as follows.

Thirty grams of powdered potassium cyanide (99—100 per cent.) and 33 grams of hydrochloric acid (sp. gr. 1·185) were added alternately in small quantities at a time to 50 grams of anisaldehyde placed in a freezing mixture. During the reaction the temperature was not allowed to rise above 10°. At the end of the addition, the mixture was extracted with ether, any unchanged aldehyde was removed by shaking the ethereal solution with a saturated solution of sodium hydrogen sulphite, and the dried ethereal extract was evaporated. The crude cyanohydrin was finally recrystallised from a mixture of benzene and light petroleum. The pure product melted at 67°.

Action of Hydrogen Chloride on Anisaldehydecyanohydrin.

As has been explained in the introduction, Minovici (*loc. cit.*), by the action of hydrogen chloride on anisaldehydecyanohydrin, obtained a compound melting at 145°, and corresponding with the formula $C_{17}H_{15}O_3N$. In carrying out the condensation, however, Minovici took no precautions to free the cyanohydrin from any admixed aldehyde. We repeated the experiment exactly as Minovici had described it, and obtained, as he did, a compound melting at 145°. We suspected that this substance was 2 : 5-di-*p*-methoxydiphenyloxazole, and confirmed our suspicions by preparing a specimen of the oxazole according to the method described by its discoverer (Minovici, *Ber.*, 1896, **29**, 2100). Mixed melting points were taken, employing the free base and also the hydrochloride; the latter was prepared in dry acetic acid solution, and melted at 195°. These experiments showed that the substance (m. p. 145°) obtained by Minovici by the action of hydrogen chloride on anisaldehydecyanohydrin was identical with 2:5-di-*p*-methoxydiphenyloxazole. The cause of its formation was the presence of unaltered anisaldehyde mixed with the cyanohydrin.

Having satisfied ourselves on this point, we next proceeded to the investigation of the action of hydrogen chloride on pure anisaldehydecyanohydrin to see if it differed in any respects from the action on benzaldehydecyanohydrin.

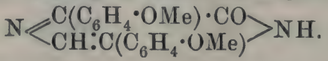
About 250 c.c. of absolute ether were saturated with dry hydrogen chloride, and to this ethereal solution, cooled in a freezing mixture, were added 10 grams of anisaldehydecyanohydrin. Great care was exercised to keep both the ether and the hydrogen chloride absolutely dry. In the presence of moisture, *p*-methoxymandelamide (m. p. 161°) (Tiemann, *Ber.*, 1881, **14**, 1976) was formed. The cyanohydrin dissolved, the solution becoming turbid after a short time, and finally a white solid was deposited. The mixture was allowed to stand overnight, the solid was collected, washed with ether, and kept on a porous plate until no more hydrogen chloride was present. The substance so obtained was a white powder, which turned pink on exposure to the air, and had a melting point varying from 110° to 132°. This powder was found to be a mixture of two substances, which were separated by means of methyl alcohol. The mixture was dissolved in the least possible quantity of this solvent, and, after some time, pale yellow needles separated. On recrystallisation from the same solvent, this substance was obtained with a melting point of 156°. It contained nitrogen, but no halogen. It exhibited no basic properties, for all attempts to prepare a hydrochloride or a picrate proved unsuccessful. The compound is very soluble in methyl alcohol, ethyl alcohol, acetic acid, or ethyl acetate:

0·1360 gave 0·3556 CO_2 and 0·0618 H_2O. $C = 71·3$; $H = 5·0$.

0·1508 ,, 6·8 c.c. N_2 (moist) at 12° and 750 mm. $N = 5·26$.

$C_{16}H_{14}O_3N$ requires $C = 71·7$; $H = 5·2$; $N = 5·2$ per cent.

3-*Keto*-2 : 5-*di*-p-*methoxydiphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,



$$N\Big\langle\begin{matrix}C(C_6H_4\cdot OMe)\cdot CO\\ CH{:}C(C_6H_4\cdot OMe)\end{matrix}\Big\rangle NH.$$

On concentrating the mother liquors after the separation of the first compound, or, better still, by saturating those mother liquors with hydrogen chloride, a substance was obtained containing chlorine and nitrogen. This substance, which is the hydrochloride of 3-keto-2 : 5-di-*p*-methoxydiphenyl-3 : 4-dihydro-1 : 4-diazine, was crystallised from alcohol saturated with hydrogen chloride, and separated in pale yellow, flat, glistening plates melting at 223°. When heated to 150°, hydrogen chloride was evolved, and the substance lost its crystalline appearance. The free base thus obtained was fairly soluble in benzene or methyl alcohol, sparingly so in ethyl alcohol or acetone, and practically insoluble in chloroform or carbon tetrachloride. After being recrystallised from benzene, it melted at 217° :

0·1399 gave 0·3602 CO_2 and 0·1399 H_2O. $C = 70·16$; $H = 5·57$.

0·1934 „ 15·6 c.c. N_2 (moist) at 16° and 738 mm. $N = 9·1$.

$C_{18}H_{16}O_3N_2$ requires $C = 70·1$; $H = 5·2$; $N = 9·1$ per cent.

The *hydrochloride* of this base was obtained directly from anisaldehydecyanohydrin. After recrystallisation from methyl alcohol saturated with hydrogen chloride, it melted and decomposed at 223°. The salt was not stable in air, and lost hydrogen chloride even when placed in a vacuum desiccator. This fact accounts for the chlorine estimations being always low and the values for nitrogen high :

0·1677 gave 0·0683 AgCl. $Cl = 10·07$.

0·1548 „ 11·3 c.c. N_2 (moist) at 16° and 748 mm. $N = 8·32$.

$C_{18}H_{17}O_3N_2Cl$ requires $Cl = 10·3$; $N = 8·13$ per cent.

The *picrate*, $C_{18}H_{16}O_3N_2,C_6H_2(OH)(NO_2)_3$.—To a quantity of the base dissolved in a small quantity of hot glacial acetic acid the theoretical quantity of picric acid, likewise dissolved in acetic acid, was added. On the addition of the picric acid, a distinct colour change was observed. As, however, no immediate precipitation took place, the solution was heated on the water-bath for about half an hour. On cooling, large, well-defined crystals belonging to the hexagonal system were deposited from the liquid. These crystals were bright yellow in colour with a green fluorescence. The substance was recrystallised from glacial acetic acid, and then melted at 131°. It contained two molecules of acetic acid of crystallisation, which are expelled at 90° :

0·1931 gave 18·2 c.c. N_2 (moist) at 14° and 738 mm. $N = 10·76$.

0·4917 lost 0·0900. Loss = 18·30.

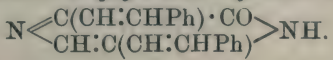
$C_{24}H_{19}O_{10}N_5,2C_2H_4O_2$ requires $N = 10·65$; $2C_2H_4O_2 = 18·26$ per cent.

The picrate freed from acetic acid melted at 183°:

0·1898 gave 21·4 c.c. N_2 (moist) at 13° and 752 mm. N = 13·18.

$C_{24}H_{19}O_{10}N_5$ requires N = 13·03 per cent.

Action of Hydrogen Chloride on Cinnamaldehydecyanohydrin. Preparation of 3-*Keto*-2 : 5-*distyryl*-3 : 4-*dihydro*-1 : 4-*diazine*,



$$N{<}\begin{matrix}C(CH{:}CHPh)\cdot CO\\ CH{:}C(CH{:}CHPh)\end{matrix}{>}NH.$$

The cinnamaldehydecyanohydrin required for these experiments was prepared according to the method described by Fittig (*Annalen*, 1899, **299**, 11).

About 200 c.c. of absolute ether were saturated with dry hydrogen chloride and cooled in a freezing mixture. Ten grams of cinnamaldehydecyanohydrin were then added. The cyanohydrin dissolved in the ether, giving a yellowish-red solution. After about three minutes, the solution became turbid and crystals were deposited. After keeping the solution overnight, the crystals were collected and preserved on a porous plate until they were free from excess of hydrogen chloride. In carrying out this condensation, it was found that a purer product was obtained by saturating the ether with hydrogen chloride before the addition of the cyanohydrin than by saturating an ethereal solution of the cyanohydrin. Further, the more dilute the solution of the cyanohydrin is, the better is the yield and the purer is the product obtained. When concentrated solutions were employed, a certain amount of tar was always formed.

The condensation product was recrystallised from the smallest possible quantity of methylated spirit or methyl alcohol. The mother liquors were saturated with hydrogen chloride, when a further yield of the substance was obtained. The compound was then heated with animal charcoal in methyl-alcoholic solution, and precipitated by saturating the solution with hydrogen chloride. On further recrystallisation from alcohol saturated from hydrogen chloride, the substance was found to melt at 259°. It was evidently the hydrochloride of a base extremely soluble in alcohol, and similar to the one obtained from anisaldehydecyanohydrin. On heating for about two hours to 150°, the hydrogen chloride was expelled and the free base was obtained and was crystallised from acetone.

3-*Keto*-2 : 5-*distyryl*-3 : 4-*dihydro*-1 : 4-*diazine* is much brighter in colour than the corresponding base obtained from anisaldehydecyanohydrin. It is very soluble in chloroform, acetone, and ethyl or methyl alcohols:

0·1208 gave 0·3520 CO_2 and 0·0620 H_2O. C = 79·5; H = 5·7.

0·1680 „ 13·7 c.c. N_2 (moist) at 14° and 748 mm. N = 9·44.

$C_{20}H_{16}ON_2$ requires C = 80·0; H = 5·3; N = 9·3 per cent.

The *hydrochloride*, $C_{20}H_{16}ON_2,HCl$, was obtained directly by the condensation of cinnamaldehydecyanohydrin. After recrystallisation from methyl alcohol, it melted and decomposed at 259°. This hydrochloride readily combines with bromine in glacial acetic acid solution:

0·1212 gave 0·0475 AgCl. Cl = 10·58.

$C_{20}H_{17}ON_2Cl$ requires Cl = 10·53 per cent.

Tetrabromide, $C_{20}H_{16}ON_2Br_4$.—The base was dissolved in chloroform (in which it is easily soluble), and the theoretical quantity of bromine, likewise dissolved in chloroform, was added. The solution became colourless, and the tetrabromide crystallised out on standing. It was recrystallised from a mixture of methyl alcohol and water, and melted at 183°.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM.

LXXVI.—*The Miscibility of Solids.*

By ERNEST VANSTONE, B.Sc. (Wales) ("Isaac Roberts" Research Scholar).

It is well known that the phenomenon of miscibility, as shown by the formation of mixed crystals, is of very frequent occurrence among the elements, whereas, at the present time, comparatively few inorganic or organic compounds are known to be miscible in the solid state. The work of Garelli and his collaborators has given us the rule "that the degree of miscibility grows as the chemical relationship between the substances becomes closer."

Nernst (*Theoretische Chemie*, p. 182) states that this rule lies hidden in buried foundations, whilst Bruni (*Feste Losungen und Isomorphismus*, p. 78) says: "The cause of this greater inclination of the elements to give solid solutions is to be sought in the often-studied influence of temperature."

Bruni also has shown that mixed crystals can be formed in three ways, namely, (1) Condensation from the mixed vapours; (2) crystallisation from the fused mixture; and (3) crystallisation from solution in a common solvent. In each of these, we are dealing with separation from a homogeneous medium.

The conditions for miscibility among compounds are as follows: (1) A close relationship in chemical constitution; (2) similarity in crystalline form; (3) nearly equal molecular volumes.

No explanation of miscibility has hitherto been suggested. The theory of Barlow and Pope, however, contains the following statement: "For an element to be isomorphously replaceable by another, their spheres of influence must be much more nearly of the same magnitude than if they are merely to possess the same valency" (Trans., 1906, **89**, 1725).

This idea is capable of development, and can be applied to the question of miscibility, as the domains of the molecules concerned constitute a very important factor.

The explanation now suggested may be stated as follows: *The greatest degree of miscibility will be shown by two compounds when their assemblages of spheres of atomic influence possess similar marshalling and are capable of being partitioned into units possessing almost equal volumes, the volumes of the units being the molecular domains.* The phenomenon of miscibility among the elements will first be considered.

Barlow and Pope have shown in their discussion of the crystalline forms of the elements (Trans., 1907, **91**, 1158) that the marshalling of the spheres of influence or the forms of molecules of the elements in the solid state are in very many cases the same. We need therefore consider only the magnitudes of the spheres of atomic influence. A comparison of the atomic volumes, and a knowledge of the valency values, afford information as to the relative sizes of these spheres. In the periodic curve of atomic volumes, most of the elements mentioned are found in the neighbourhood of the minima, and the minima occur at points of approximately equal atomic volumes. Thus the atomic volumes of the elements do not in general differ very widely from one another.

Generally speaking, then, the conditions for miscibility are satisfied in the case of the elements.

Experimental evidence is obtained from the freezing-point curves of pairs of elements. In table I (page 592), pairs of elements are arranged in the same horizontal row. The freezing-point curve for each is continuous, and we conclude that the elements are miscible in all proportions.

The elements in the same horizontal row in table I crystallise in the same system, and, as is shown, have nearly equal atomic volumes. A third important factor is the correspondence in valency values. The condition for miscibility among the elements may be stated as follows:

"Two elements will show the greatest degree of miscibility when they possess spheres of atomic influence of nearly the same volume, provided they crystallise in the same system."

The elements in the same horizontal row of table II form two

TABLE I.

Element.	Atomic volume.	Valency.	Element.	Atomic volume.	Valency.
Cl	26·5	1	Br	26·7	1
Br	26·7	1	I	25·5	1
S	15·4α 16·2β	2	Se	16·4 to 18·5	2
Se	16·4 to 18·5	2	Te	20·4	2
Cu	7·1	1 or 2	Pd	9·3	2 or 4
Cu	7·1	1 or 2	Pt	9·0	2 or 4
Ag	10·2	1	Au	10·2	1 or 3
Ag	10·2	1	Pd	9·3	2 or 4
Au	10·2	1 or 3	Pt	9·0	2 or 4
Au	10·2	1 or 3	Pd	9·3	2 or 4
Mg	13·8	2	Cd	12·8	2
Cd	12·8	2	Hg	14·6	1 or 2
Hg	14·6	2	Sn	16·2	2 or 4
Sb	18·0	3	Bi	21·2	3
Fe	7·2	2 or 3	Cr	7·5	2 or 3
Fe	7·2	2 or 3	Mn	7·3	2 or 4
Fe	7·2	2 or 3	Co	6·9	2 or 4
Fe	7·2	2 or 3	Ni	6·6	2 or 4
Fe	7·2	2 or 3	Pt	9·0	2 or 4
Mn	7·3	2 or 4	Cu	7·1	2 or 4
Mn	7·3	2 or 4	Co	6·9	2 or 4
Mn	7·3	2 or 4	Ni	6·6	2 or 4
Co	6·9	2 or 4	Ni	6·6	2 or 4

series of mixed crystals. The freezing-point curve is characterised by a single eutectic point, and on either side of it, solid solutions exist. The degree of miscibility is now lower than that of the elements in table I.

TABLE II.

Element.	Atomic volume.	Valency.	Element.	Atomic volume.	Valency.
P	14·7 white 16·8 red	3	S	15·4α 16·2β	2
Cu	7·1	1 or 2	Zn	9·1	2
Cu	7·1	1 or 2	Fe	7·1	2 or 3
Cu	7·1	1 or 2	Co	6·9	2 or 4
Cu	7·1	1 or 2	Ni	6·6	2
Cu	7·1	1 or 2	Ag	10·0	1
Cu	7·1	1 or 2	Au	10·2	1 or 3
Ag	10·0	1	Zn	9·1	2
Tl	17·2	1 or 3	Pb	18·1	2 or 4

A study of this table again shows that correspondence in atomic volumes and also in valency values are the determining factors. The differences between the atomic volumes are now greater than they were in table I. It must be pointed out that the crystal forms of compounds have, up to the present time, not been sufficiently investigated for the proper valency values to be assigned to the elements, hence the use of more than one number in the tables. The elements in table III do not form mixed crystals, the freezing-point curve has a single eutectic point.

TABLE III.

Element.	Atomic volume.	Valency.	Element.	Atomic volume.	Valency.
Cu	7·1	1 or 2	Bi	21·2	3
Tg	10·2	1	Pb	18·1	2 or 4
Au	10·2	1 or 3	Tl	17·2	1 or 3
Au	10·2	1 or 3	Ni	6·6	2
Zn	9·2	2	Cd	12·8	2
Pb	18·3	2	Sb	18·0	3
Cd	12·8	2	Tl	17·2	1 or 3
Na	23·0	1	K	46·0	1

The differences in atomic volumes now are very much greater with the single exception of lead and antimony. In this case the two elements have not the same arrangement of the atoms in their respective molecules, as lead crystallises in the cubic system and antimony in the hexagonal.

The Miscibility of Compounds.—The notion of marshalling now becomes more prominent, as we are dealing with different atoms, or spheres of different magnitudes, and the form of the molecule depends on the mode in which these are marshalled. Similarity in marshalling is indicated by a close relation between the structural formulæ of the compounds, and by correspondence in crystalline form. The following table contains in the same horizontal row pairs of compounds which are miscible in all proportions:

TABLE IV.

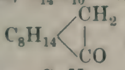
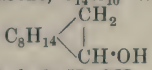
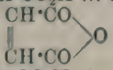
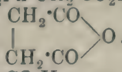
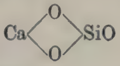
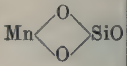
Compound.	Compound.	Difference in valency volume.
Anthracene, $C_{14}H_{10}$	Phenanthrene, $C_{14}H_{10}$	0
Camphor,  $C_8H_{14}\left\langle\begin{array}{l}CH_2\\ \vert\\ CO\end{array}\right.$	Borneol,  $C_8H_{14}\left\langle\begin{array}{l}CH_2\\ \vert\\ CH{\cdot}OH\end{array}\right.$	2
Naphthalene, $C_{10}H_8$	β-Naphthol, $C_{10}H_7{\cdot}OH$	2
p-Dichlorobenzene, $C_6H_4Cl_2$	*p*-Dibromobenzene, $C_6H_4Br_2$	0
Cinnamic acid, $CHPh{:}CH{\cdot}CO_2H$	β-Phenylpropionic acid, $CH_2Ph{\cdot}CH_2{\cdot}CO_2H$	2
Maleic anhydride,  $\left.\begin{array}{l}CH{\cdot}CO\\ \Vert\\ CH{\cdot}CO\end{array}\right\rangle O$	Succinic anhydride,  $\left.\begin{array}{l}CH_2{\cdot}CO\\ \vert\\ CH_2{\cdot}CO\end{array}\right\rangle O$	2
Stearic acid, $C_{17}H_{35}{\cdot}CO_2H$	Elaidic acid, $C_{17}H_{33}{\cdot}CO_2H$	2
Dibenzyl, $CH_2Ph{\cdot}CH_2{\cdot}Ph$	Stilbene, $CHPh{:}CHPh$	2
Fluorene, CH_2Ph_2	Stilbene, $CHPh{:}CHPh$	4
Azobenzene, $NPh{:}NPh$	Stilbene, $CHPh{:}CHPh$	4

TABLE V.

Inorganic compounds.	Inorganic compounds.	Difference in valency volume.
Mercuric bromide	Mercuric iodide	0
Antimony tribromide	Arsenic tribromide	0
Potassium sulphate	Potassium chromate	0
Calcium disilicate,  ..	Manganese disilicate, 	0
Magnesium sulphate	Ferrous sulphate	0
Potassium alum	Chrome alum	0

In all cases we observe close relationship in constitution, and almost identical valency volumes. It is obvious that a close agreement must also exist between the molecular volumes, as volume is mainly an additive property, and the compositions of the molecules are almost identical.

It will be seen from table IV that two compounds, the valency volumes of which differ by two units, may yet be miscible in all proportions. This means that the addition of two unit or hydrogen spheres to the group of spheres representing the molecule of cinnamic acid, say, does not alter to any great extent the volume occupied by that group. This explanation is also suggested in the Barlow and Pope theory, as the following quotation shows:

"The geometrical peculiarities, which are the analogues of an ethylenic and an acetylenic bond, suggest that the spheres between which the double or triple bond is operative are not closely surrounded by other spheres, and that when a carbon sphere is in a state of saturated combination, the shell of spheres enveloping it will be found to have a maximum density of packing" (Trans., 1906, **89**, 1744).

The work of Kopp and Thorpe on molecular volumes has shown that the grouping ⁚C·C⁚ occupies a greater volume than ⁝C·C⁝, and this supports the above explanation. It has been pointed out by Barlow and Pope that a change in the molecular volume of a compound caused by the substitution of one atom by another, as hydrogen by chlorine, means an expansion or contraction of the molecule uniformly in all directions. The removal, then, of two hydrogen spheres from the saturated molecule is accompanied by an expansion of the remaining spheres, whereby the change in volume is to some extent compensated. Precisely the same explanation applies to the oxidation of the ·CH·OH group to ·CO, and, conversely, the addition of two hydrogen spheres or the process of reduction is accompanied by a shrinking of the other spheres already present: this is the interpretation of Kopp's statement that the atomic volume of oxygen in carbon monoxide is greater than oxygen in the hydroxyl group. The perfect miscibility of camphor and borneol is thus explained, the volume occupied by the spheres of atomic influence constituting the space unit of the camphor molecule is very nearly equal to that occupied by the spheres constituting the space unit of the molecule of borneol. Again, the work of Kopp and Thorpe has shown that different changes in the molecular volume take place when the substituting atom or group enters different positions in the benzene nucleus; the ortho-substituted compounds have the least molecular volumes, and the para-compounds the greatest. The same phenomenon occurs in connexion with substitution in the naphthalene ring, and the perfect miscibility of β-naphthol and naphthalene may be accounted for by saying that the addition of an oxygen sphere does not produce any great change in volume if it enters the β-position in the naphthalene ring, a greater change occurring if the oxygen atom enters the α-position. The assumption of a double linking between the two carbon atoms in the β-positions provides another possible explanation.

The term "isomorphism" has been omitted in the preceding discussion, because various interpretations of the word are current.

EXPERIMENTAL.

Of solid substances possessing a vapour pressure susceptible of accurate measurement, camphor stands out prominently; hence is was suggested to me by Dr. E. P. Perman that I should search for a substance capable of forming solid solutions with camphor, and from determinations of the vapour pressures of the pure substance and of its dilute solid solutions obtain values for the molecular weight of camphor in the solid state by the application of Raoult's Law. This work led me to consider the relation between crystalline form and chemical constitution, and hence to a study of the theory of Barlow and Pope, resulting in the development of the preceding views of miscibility.

Camphor crystallises in hexagonal prisms, capped by pyramids, and, of the closely related derivatives, borneol or hydroxycamphor crystallises in hexagonal plates.

A comparison of the structural formulæ shows that the relationship between these two compounds is an extremely close one. The molecular volumes have been determined by Kuhara (*Amer. Chem. J.*, 1889, **11**, 244), with the following results:

Camphor	Molecular volume	187·42
Borneol	,, ,, ...	190·5

We thus have three indications that borneol will probably form mixed crystals with camphor.

Preparation of Mixed Crystals from Solution.—Mixed crystals were obtained by the spontaneous evaporation of solutions of these substances in alcohol, toluene, and light petroleum.

The crystals from alcoholic solution were small, and appeared homogeneous when examined microscopically, although no definite shape could be distinguished; those from light petroleum were large, thin plates similar to thin plates of ice, and those from toluene were small, fern-like crystals.

Approximately equal quantities of the substances were dissolved in each case, and the melting points of the mixed crystals, determined by means of capillary tubes, were always intermediate between the melting points of camphor and borneol.

Mixed Crystals prepared by Fusion and Subsequent Solidification.—Mixtures in varying proportions were fused in sealed tubes, the tubes allowed to cool, the solid mass removed, and its melting point taken in the usual manner.

In each case the melting point of camphor was raised, the elevation being approximately proportional to the quantity of borneol present.

Investigation of the Freezing-point Curve.—The preliminary experiments described clearly indicate that borneol and camphor form solid solutions, and an accurate investigation of the freezing points of a series of mixtures was next attempted.

This was found to be a task of considerable difficulty, for the following reasons:

(1) The comparatively high temperature of the melting points, namely, 178—208°.

(2) The great volatility of the compounds at those temperatures.

(3) The substances char if kept for any length of time in the fused state; hence all determinations must be made as rapidly as possible.

The melting points of the pure substances were determined as follows: A glass tube, rather longer than a test-tube and of somewhat thicker glass, contained about five grams of the substance. The tube was provided with a stirrer made of stout copper wire. An Anschütz normal thermometer, filled with nitrogen and having a range of 140° to 215°, was used. This thermometer was graduated in fifths of a degree. It was standardised by suspending it in the vapours of suitable liquids, boiling at atmospheric pressure, and was found to be correct to within 0·1°. The thermometer being only six inches long, passed almost entirely within the tube, being kept in position by means of an ordinary cork, bored so as to take thermometer and stirrer.

By immersing the tube almost to its mouth in the bath, condensation of the camphor took place only at the mouth, and did not obscure the mercury thread.

The outer bath consisted of a large boiling tube nearly filled with olive oil, and was also provided with a copper stirrer. The bath was heated directly by means of an ordinary Bunsen burner. It was found convenient to illuminate the bath of oil by means of an incandescent burner placed behind it.

The same apparatus was adopted in the determination of the freezing points of mixtures. To prevent volatilisation as far as possible, a tightly fitting cork was used and pushed well into the tube; in this way the only means of escape for the vapour was through the small hole through which the stirrer passed, and through the pores in the cork. In all cases a small quantity escaped, but its effect was considered to be negligible, as about five grams of substance were used. In order to increase the rapidity of the experiment and minimise the effect caused by charring, the substances were weighed out in glass tubes, on the ends of which bulbs had been blown, the other ends were then sealed; the substances were fused by heating the bulb with an ordinary burner and mixed thoroughly by shaking the tube. It was not found possible to determine the melting points of the mixtures, as the substances pass through a translucent state, and hence the temperature at which melting begins could not be accurately observed.

The freezing points could, however, be observed with precision, as the temperature remained constant for a short time, when the greater part of the substance solidified; superfusion was not observed in any of the determinations.

The Freezing Points of Mixtures of Camphor and Borneol.

Weight of camphor.	Weight of borneol.	Percentage of borneol.	Freezing point.
Pure camphor	—	—	178·5° 178·6 178·8
4·5938	0·5147	9·9	181·7 182·0 182·0
3·9396	1·0104	20·2	185·4 185·6 184·8

The Freezing Points of Mixtures of Camphor and Borneol (continued).

Weight of camphor.	Weight of borneol.	Percentage of borneol.	Freezing point,
3·5782	1·5783	30·3 …………	189·4
			189·0
			188·8
			189·0
			189·0
2·9788	1·9982 *l*-borneol	39·8 …………	191·0
			191·0
			191·0
			191·4
2·5794	2·4200	48·0 …………	194·8
			195·0
			195·0
			194·8
			195·0
2·0316	3·5128	63·0 …………	199·6
			199·6
			199·4
			199·6
2·2367	4·7728	67·8 …………	200·3
			200·3
			200·4
1·0214	4·0138	79·5 …………	203·4
			203·5
			203·4
			203·4
0·5040	4·6970	90·0 …………	206·4
			206·2
			205·8
			205·8
2·9950	2·0188 borneol	40·0 …………	192·6
			192·4
			192·2
			192·3
2·0082	3·0288	59·8 …………	198·4
			198·6
	Pure *d*-borneol (Kahlbaum's) ……		208·6
	l-Borneol (Schimmel's) …………		206·8
			206·8

The melting points of camphor and borneol obtained from various sources have been determined by Haller (*Ann. Chim. Phys.*, 1892, [vi], **27**, 392). The following are his results:

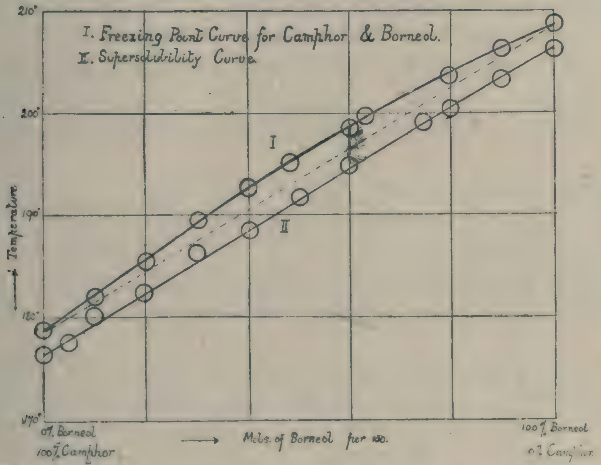
Camphor. Melting point.	Borneol. Melting point.
178·4°	208·4°
178·2	208·8
178·6	208·0
178·5	208·6
	209·0
Mean … 178·4	
	Mean … 208·5

The various freezing points have been plotted on a temperature-concentration diagram, Fig. 1. The curve obtained is of the same form as that obtained by Miers and Isaac (Trans., 1908, **93**, 927) for mixtures of naphthalene and β-naphthol, and is conclusive proof that camphor and borneol form a continuous series of solid solutions.

The freezing points of the pure substances and of their mixtures were also determined by means of capillary tubes attached to the thermometer and immersed in a boiling tube containing olive oil. To prevent volatilisation, the walls of the capillary tube were caused to fall together by heating in a small flame at a point below the open end; the sealed portion of the tube was then completely immersed in the oil.

In this way the temperature of spontaneous crystallisation is determined, and the curve shown in Fig. 1 corresponds with that obtained by Miers and Isaac for naphthalene and β-naphthol.

FIG. 1.



It seems, therefore, that the freezing points usually obtained are the temperatures of supersolubility.

Specific Rotations of Camphor and Borneol.—In order to test the purity of the camphor and borneol used, observations of their rotatory power were made.

The following results were obtained, using a 2-dcm. tube; column 2 contains those calculated from Landolt's formula:

$$[\alpha]_D^{20^\circ} = 54{\cdot}38 - 0{\cdot}1614\,q + 0{\cdot}000369\,q^2.$$

where q = percentage of solvent in solution.

I. $[\alpha]_D^{10^\circ}$.	II. $[\alpha]_D^{20^\circ}$.	q.
+43·98	+43·68	81·43
+43·77	+43·35	84·69
+43·40	+42·74	88·79

The following values for the specific rotation of borneol were obtained.

Borneol.	$[\alpha]_D^{10°}$.	Haller's results (*loc. cit.*).
13·23	+27·63	+37·33
13·37	27·07	−37·77
14·54	27·57	−37·77
15·06	26·87	−38·20
15·39	27·12	—
18·38	28·00	—
21·79	28·14	—
17·80	29·01 in toluene solution.	

Dr. H. O. Jones, of Cambridge, was kind enough to supply me with some *l*-borneol prepared by Schimmel; its melting point was constant at 206·8°, whereas Kahlbaum's borneol melted at 208·6°. Determinations of the specific rotation of the *l*-borneol gave the values −35·65 and −35·75 in alcohol solution at about 12°. A mixture of camphor and *l*-borneol containing 39·7 per cent. of the latter solidified at 191°. These results show that Kahlbaum's borneol is partly racemised, and Schimmel's *l*-borneol contains some impurity.

The case of camphor and borneol is, I think, the first found in which a ketone is capable of forming solid solutions with its corresponding secondary alcohol. In order to determine whether such miscibility was the general behaviour of these two classes of compounds, other pairs of ketones and alcohols have been investigated.

The case of benzoin and benzil was thought to be a suitable one. These substances crystallise in the same system and are related in the same manner as camphor and borneol. The freezing points were determined by the method already described, but the difficulties encountered with camphor and borneol were now absent.

The following results were obtained:

Weight of benzil.	Weight of benzoin.	Percentage of benzoin.	Freezing point.
Pure benzil	—	0·0	94·4°
			94·4
			94·2
			94·3
3·4408	0·3120	8·2	89·7
			89·7
3·2646	0·6166	15·7	85·3
			85·4
			85·5
3·8188	0·8324	17·7	84·1
4·5248	1·5021	24·7	84·2
4·5474	1·7210	27·2	84·2
			84·6
			84·3
			84·5

Weight of benzil.	Weight of benzoin.	Percentage of benzoin.	Freezing point.
3·8646	1·7172	30·5	89·6
4·2674	2·5320	37·0	96·5
3·3988	2·2526	39·6	99·0
			99·4
			99·1
3·401	3·3012	49·0	106·2
2·1180	2·2066	50·7	107·5
			107·0
2·0781	3·0164	59·0	113·4
			113·0
2·1494	2·2134	60·5	113·6
4·3916	2·4272	64·7	116·2
1·2078	3·9069	76·2	122·8
			122·2
			121·8
1·0092	4·0184	79·7	124·6
0·6108	4·5778	88·1	128·4
0·3086	3·4696	91·7	128·7
			128·6
			128·4
Kahlbaum's pure benzoin......................		100·0	132·8
			132·5
			133·2
Pure benzoin, seven times recrystallised...		—	133·2

In these experiments it was observed that the temperature fell several degrees below the freezing point given above, but rose rapidly to that value as a mass of crystals separated; the mixture, however, did not solidify completely, but remained partly liquid until the temperature had fallen below that indicated by the point of intersection of the curves in the diagram; the mercury then rose again, remaining constant at the temperature of the horizontal portion, namely, 84·2°, while complete solidification occurred.

All mixtures containing from 17 to 65 per cent. of benzoin behaved in this manner.

Mixtures with quantities of benzoin beyond these limits solidified completely within a much smaller range of temperature.

A mixture of benzoin and benzil in the proportions indicated by the point of intersection of the curves was found to solidify at 84·2°. The temperature remained quite constant, while the whole mass solidified.

A mixture containing 17·8 per cent. of benzoin partly solidified at 84·1°, this being the maximum temperature observed while the partial solidification occurred; the temperature then fell slowly until the remainder solidified, when it rose to 84·0°.

Thus the temperature corresponding with the point of intersection of the curves was not reached, a horizontal portion of the curve being obtained in the neighbourhood of that point.

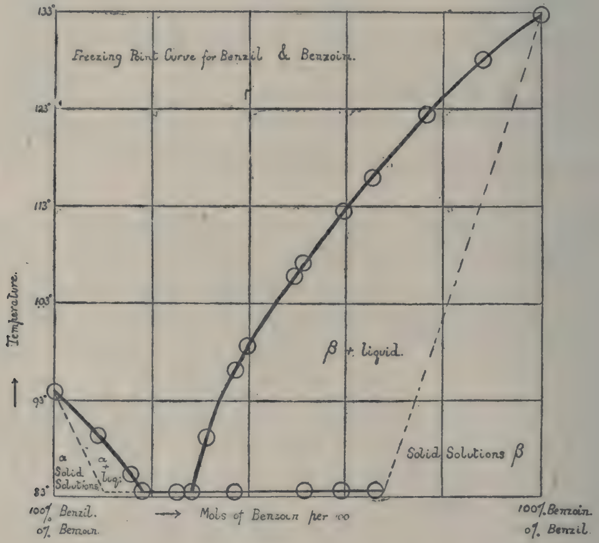
Determinations of the melting points of the mixtures in capillary tubes showed that mixtures which exhibit the second freezing point, 84°, begin to melt at that temperature.

The equilibrium diagram for benzil and benzoin is thus nearly complete. It is probable that the curve of liquid solubility intersects both branches of the liquidus, and that this is the cause of the horizontal portion.

Separation into two liquid layers could not be observed, as the liquid was constantly stirred during the experiment.

The diagram (Fig. 2) is similar to that for metals which are partly soluble in each other, both when just liquid and when just solid. It shows clearly that two series of solid solutions are formed.

FIG. 2.



On the left, we have solid solutions richer in benzil, and, on the right, solid solutions richer in benzoin. These are denoted by α and β in the diagram.

Eutectic points occur at 84° and at concentrations of 17·8 and 27·2 per cent. of benzoin respectively. As benzil possesses a symmetrical molecule, whereas benzoin is unsymmetrical, a pair of substances more closely analogous to camphor and borneol was investigated, namely, menthol and menthone. Menthone is a liquid at the ordinary temperature, and I was unable to find that any determination of its freezing point had yet been made. It was, however, frozen by immersion in a bath of solid carbon dioxide and ether. A temperature of −50° had to be obtained before solidification occurred.

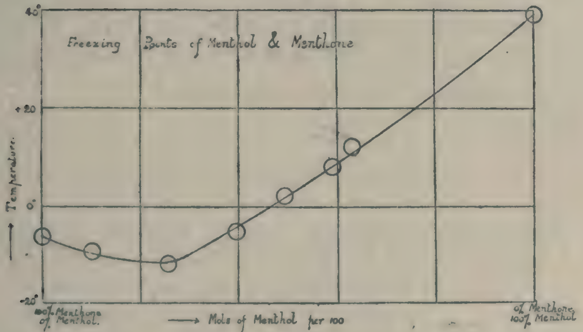
The substance remained solid until −6·6° was reached; fusion then took place, the temperature remaining constant. It was again frozen before all the crystals had melted, and the temperature was again constant at −6·6°.

Mixtures were then made and caused to freeze in the bath of solid carbon dioxide and ether.

The temperatures were taken by means of a pentane thermometer graduated in degrees, and having a range of −100° to 50°. The results are believed to be correct to within 0·5°.

Weight of menthone.	Weight of menthol.	Percentage of menthol.	Freezing point.
Pure	—	0·0	−6·6°
6·3393	0·7334	10·2	−9·1
9·4383	3·2756	25·5	−12·0
9·4383	6·2756	39·6	−5·0
9·4383	9·2756	49·2	+2·0
9·4383	12·2756	56·2	+8·0
9·4383	16·2756	63·0	+12·0
—	Pure	—	+39·0

FIG. 3.



The freezing points have been plotted on a temperature-concentration diagram (Fig. 3). A sufficient number of mixtures in the neighbourhood of the minimum point has not been investigated to enable one to decide whether the curve is a continuous one with a minimum point or whether it consists of two intersecting curves.

Summary.

(1) The theory of Barlow and Pope suggests that a close similarity in marshalling of the spheres of atomic influence, and equivalence in molecular and valency volumes, explains the miscibility of compounds, both organic and inorganic.

(2) The same explanation applies to the miscibility of the

elements; the great tendency of these to form mixed crystals is due to the fact that the majority of them crystallise in the hexagonal and cubic systems, and have atomic volumes not very different from one another.

(3) The freezing-point curves for camphor and borneol, benzil and benzoin, menthone and menthol, have been investigated. The first pair of substances form a continuous series of mixed crystals, the addition of borneol raising the freezing point of camphor. The curve for benzil and benzoin has two eutectic points, with a horizontal portion between; two series of mixed crystals are also formed.

In conclusion, it may be stated that determinations of the vapour pressures of camphor by two methods have been made, and similar work on the vapour pressures of borneol and of mixed crystals of camphor and borneol is in progress.

The expenses in connexion with the work have been defrayed by a grant from the Education Committee of the Glamorgan County Council, for which I wish to express my thanks.

I am also very grateful to the staff of the Chemical Department of University College, Cardiff, and especially to Dr. E. P. Perman for his constant guidance, kindly advice, and encouragement.

UNIVERSITY COLLEGE,
CARDIFF.

LXXVII.—*Some Esters of Antimony Trioxide.*

By JOHN FRANCIS MACKEY.

IN a previous paper, Lang, MacKey, and Gortner (Trans., 1908, **93**, 1364) described a method for the esterification of arsenious oxide with the fatty alcohols and with phenol and its homologues by removing the water produced by the reaction:

$$6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O$$

as quickly as it was formed by means of anhydrous copper sulphate placed in a Soxhlet tube attached to a flask containing weighed quantities of the reacting substances. By this means a large number of esters, which other methods had failed to produce, were prepared in quantity, and found to correspond with the general formula R_3AsO_3. In the present work, attempts were made to form the corresponding esters of antimony by five different methods, namely: (1) heating a mixture of the alcohol and antimony trioxide in a flask to which a reflux condenser was attached; (2) heating a mixture of the alcohol and antimony trioxide in a sealed tube at 150°; (3) shaking a mixture of the alcohol and antimony trioxide with anhydrous copper sulphate in the cold; (4) heating a mixture of the alcohol and antimony trioxide in a flask with a Soxhlet tube, filled with anhydrous copper sulphate, attached; (5) heating a mixture of the alcohol, antimony trioxide, and calcium turnings in a flask with reflux condenser. A comparison of the yields obtained is given in the sequel. By means of these methods, and more particularly the last two, esters were formed with methyl, ethyl, propyl, *iso*butyl, amyl, and *iso*amyl alcohols; also with phenol, *o*, *m*-, and *p*-cresols. The esters were found to correspond with the general formula R_3SbO_3. In all cases the yields obtained with antimony trioxide were very much lower than the corresponding arsenites previously described.

EXPERIMENTAL.

(i) *Heating with reflux condenser only.*—Weighed quantities of methyl, ethyl, propyl, *iso*butyl, amyl, and *iso*amyl alcohols were mixed with an excess of antimony trioxide, and heated for different periods of time in a flask to which a reflux condenser was attached. After five hours' heating not a trace of ester could be detected in any of the reacting mixtures; but, after fifteen hours' heating, evidence was obtained that, in the case of *iso*butyl and *iso*amyl alcohols, esters were formed, but not in quantities sufficient to permit of their being isolated. That an ester was formed was shown by pouring the clear liquid into water-free benzene,* in which antimony trioxide is very sparingly soluble, and filtering. By this means any antimony trioxide merely dissolved in the alcohol was separated, and, if antimony were found in the above filtrate, it must have been present in the form of an ester. The filtrate gave a distinct precipitate of antimony sulphide when acidified, treated with hydrogen sulphide, and warmed; thus, whilst there is no doubt that both *iso*butyl and *iso*amyl antimonites are formed under these conditions, the yields are so small that it is impossible to isolate them by fractional distillation.

(ii) *Heating in sealed tubes.*—Quantities of the various alcohols were mixed with antimony trioxide and heated for six hours in sealed tubes at 150°, but in no case could the presence of any ester be detected.

(iii) *Using a dehydrating agent in the cold.*—Weighed quantities of the various alcohols were mixed with antimony trioxide and a considerable amount of anhydrous copper sulphate. The mixture was then placed in a shaking machine for three days at room temperature. In the case of *iso*butyl and *iso*amyl alcohols, esters were formed, but not in quantities sufficient to enable them to be isolated.

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* Great difficulty was found in obtaining benzene absolutely free from water. The samples of benzene at hand were found to contain enough water to decompose partly the esters formed. It was necessary to heat the benzene with calcium turnings for about forty-eight hours.

(iv) *Heating with Soxhlet attachment and anhydrous copper sulphate.*—Thirty grams of antimony trioxide were added to 160 grams of *iso*amyl alcohol in a 250 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate; the mixture in the flask was heated to boiling, and the water formed by the reaction was absorbed by the copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was continued for about fifteen hours; after cooling, the clear product was poured off from the antimony trioxide and fractionated under diminished pressure. About 10·8 grams of the ester were formed, representing a yield of 13·62 per cent.

By this method esters were formed with methyl, ethyl, propyl, *iso*butyl, amyl, and *iso*amyl alcohols, as shown in the following table:

Table of yields by various methods.

Ester.	Reflux condenser.	In sealed tubes.	Anhydrous copper sulphate. In the cold.	Anhydrous copper sulphate. In Soxhlet.
Methyl	nil	nil	nil	8·09 per cent.
Ethyl	,,	,,	,,	3·00* ,,
Propyl	,,	,,	,,	13·3 ,,
*iso*Butyl	trace	,,	trace	15·11 ,,
Amyl	nil	,,	nil	13·16 ,,
*iso*Amyl	trace	,,	trace	13·62 ,,

* It will be noticed that the same extremely low yield of ester with ethyl alcohol occurred in the preparation of the esters of arsenious acid, described in a former paper, where a possible explanation was advanced.

These esters were purified and analysed, the following methods of analysis being employed.

Method of analysis for esters of the aliphatic alcohols (using iso*amyl antimonite as an example).*—Two methods were employed for the determination of the antimony. In the first method, iodine was used to oxidise the trioxide to the pentoxide, but was not found to give accurate results, so that the following procedure was adopted.

1·0057 Grams of the ester were decomposed by 5 c.c. of concentrated hydrochloric acid, 50 c.c. of tartaric acid solution were added, and the antimony was precipitated from this solution by means of hydrogen sulphide; the antimony sulphide thus formed was converted into antimony tetroxide by treatment with fuming nitric acid and ignited:

1·0057 gave 0·4024 Sb_2O_4. Sb = 31·57.

$C_{15}H_{33}O_3Sb$ requires Sb = 31·48 per cent.

This method of analysis gave the following results:

Ester.	Percentage of Sb found.	Percentage of Sb calculated from the formula R_3SbO_3.
Methyl	56·68	56·41
Ethyl	—	47·41
Propyl	40·29	40·40
*iso*Butyl	35·37	35·40
Amyl	31·44	31·48
*iso*Amyl	31·34	31·48

Expressing these as salts of antimonous acid, we arrive at the general formula R_3SbO_3 for them.

Properties of the Esters of the Aliphatic Alcohols with Antimony Trioxide.

Methyl antimonite is a colourless liquid, b. p. 65°, sp. gr. 1·025.

Ethyl antimonite is a colourless liquid, b. p. 115—120°.

Propyl antimonite is a yellow liquid, sp. gr. 1·042, b. p. 143°/30 mm.; at atmospheric pressure it decomposes into propyl alcohol and antimony trioxide at 200°.

iso*Butyl antimonite* is a yellow, mobile liquid, sp. gr. 1·058, b. p. 144°/30 mm.; it decomposes into *iso*butyl alcohol and antimony trioxide at 250° under atmospheric pressure.

Amyl antimonite is a yellow liquid, sp. gr. 1·079, b. p. 170°/30 mm.

iso*Amyl antimonite* is a yellow, mobile liquid, sp. gr. 1·081, b. p. 163°/30 mm.; at 250°, under atmospheric pressure, it decomposes into antimony trioxide and *iso*amyl alcohol.

All these esters are readily soluble in absolute alcohol, ether, chloroform, or benzene, but decompose immediately on addition of water into antimony trioxide and the alcohol from which they were prepared.

The fifth method was not employed for the aliphatic alcohols.

Esters obtained with Phenol and its Homologues.

For the esterification of these substances with antimony trioxide, two method were used, namely, heating the mixture of phenol and antimony trioxide in a flask to which a Soxhlet apparatus containing anhydrous copper sulphate was attached, and heating the mixture of phenol and antimony trioxide with calcium turnings in a flask under a reflux condenser. By these means esters were obtained with phenol, *o*-, *m*-, and *p*-cresols. In the case of phenol and *m*-cresol, unsuccessful attempts to obtain the esters were made by heating these materials with antimony trioxide with a reflux condenser only.

Phenyl antimonite.—One hundred and twenty-five grams of phenol and 25 grams of antimony trioxide were heated in a flask fitted with a Soxhlet apparatus containing anhydrous copper sulphate. Clouds of steam began to form at 100°, indicating that the reaction began at that temperature; the thermometer rose very quickly to the boiling point of phenol, and remained very close to that temperature (varying from 170° to 180°) for about seven hours, when the temperature gradually rose, and, after fifteen hours' heating, reached a maximum of 290°. This maximum is the highest temperature to which the ester can be heated without decomposition. The mixture of phenol, ester, and antimony trioxide was then shaken with water-free benzene, causing the precipitation of the antimony trioxide dissolved in the ester and in the phenol, and, after filtering, fractionated under diminished pressure. The benzene distilled at 30°, phenol at 70°, and the ester at 250°.* The ester was purified by dissolving in benzene, filtering from any antimony trioxide, and separating by passing a current of hot, dry air over the benzene solution placed in a vacuum desiccator. The crystals thus obtained had no very definite melting point owing to the presence of some phenol. To remove the latter, the crystals were heated to 200° for twenty minutes, dissolved in benzene, filtered, and crystallised as before. The crystals thus obtained were light brown in colour, and melted at 13°. At 18°, *phenyl antimonite* has a specific gravity of 1·621, and boils at 250°/30 mm. It dissolves readily in absolute alcohol, ether, chloroform, or benzene, and decomposes on addition of water into phenol and antimony trioxide. On analysis, it was found to correspond with the formula $(C_6H_5)_3SbO_3$ or $(C_6H_5O)_3Sb$. This ester was also prepared by heating a mixture of phenol, antimony trioxide, and calcium turnings in a flask fitted with a reflux condenser. By this method, a yield of 62 per cent. was obtained after two hours' heating. By the former method the yield is not more than 40 per cent. after fifteen hours' heating.

o-, m-, and p-*Tolyl Antimonites.*—One hundred and fifty grams of each of the cresols were heated with about 30 grams of antimony trioxide, using the methods described above. The excess of antimony trioxide was separated by means of benzene, filtered, and the esters fractionated. After purification they were analysed, and found to correspond with the formula $(C_6H_4{\cdot}CH_3)_3SbO_3$ or $(C_6H_4{\cdot}CH_3{\cdot}O)_3Sb$. o-*Tolyl antimonite* crystallises in dark brown masses, and melts at 16°; its specific gravity is 1·480, and it boils at 352°. m-*Tolyl antimonite* is a yellow liquid, with a specific gravity of 1·475, and boils at 300°/30 mm. p-*Tolyl antimonite* is a dark brown, crystalline solid, melts at 14°, has a specific gravity of 1·495, and boils at 345°/30 mm.

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* Even at 250° the ester suffers partial decomposition.

Whilst in the case of the aliphatic alcohols a drying agent in the Soxhlet apparatus was essential to absorb the water formed and allow the alcohols only to drop back into the mixture, no drying agent was necessary with the phenols, as practically no phenol or ester ever found its way further than the side-tube of the Soxhlet.

The water formed remained in the Soxhlet, there being never sufficient volume of water produced to cause the syphon attachment to come into play. The use of metallic calcium, it will be noticed, gave a better yield of ester than the Soxhlet method.

Method of Analysis of Phenyl and Tolyl Esters.—To 1·5960 grams of phenyl antimonite, 5 c.c. of potassium hydroxide (containing 7 grams per 10 c.c.) were added, and then an excess of tartaric acid. The excess of tartaric acid was neutralised by sodium carbonate, and 25 c.c. of sodium hydrogen carbonate added. The whole was diluted to 500 c.c., and two samples of 20 c.c. each were taken for analysis. To each, 20 c.c. standard iodine was added in excess (shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution), the temperature being kept at 65°. The mixture was then cooled, acidified with dilute sulphuric acid, and diluted with water to 500 c.c. The tri-iodophenol was filtered off, and the excess of iodine in 100 c.c. of the filtrate was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine that was in excess. This quantity, subtracted from the original amount of the iodine added, gave the amount necessary to change both the phenol to tri-iodophenol and the antimony trioxide to antimony pentoxide.

Owing to the presence of tartaric acid in the above, it was impossible to estimate at all accurately the antimony trioxide by means of dichromate. The method previously described under *iso*amyl antimonite, namely, weighing the antimony as antimony tetroxide, was used. The percentage of antimony, as determined in this way, was found to be 30·10. The strength of the iodine being known, the number of c.c. of iodine equivalent to 30·10 per cent. of antimony was subtracted from the iodine obtained in the previous determination, the difference being the amount combined with phenol.

To test the accuracy of this method, estimations were made with weighed quantities of (*a*) phenol, (*b*) antimony trioxide, (*c*) a mixture of these.

(*a*) To 0·8826 gram of phenol, 5 c.c. of a solution of potassium hydroxide (7 grams per 10 c.c.) were added, and the whole diluted with water to 250 c.c. ... ... (1)

10 c.c. of this solution were equivalent to 28·90 c.c. of iodine.

(*b*) To 0·5000 gram of antimony trioxide were added 25 c.c. of a saturated solution of tartaric acid; sufficient sodium carbonate to neutralise the excess of the tartaric acid and 50 c.c. of sodium hydrogen carbonate were then added, and the whole diluted with water to 500 c.c. ... ... (2)

100 c.c. of this solution were equal to 13·70 c.c. of iodine.

(*c*) To 10 c.c. of (1) were added 100 c.c. of (2), and together required 42·45 c.c. of iodine.

Thus 100 c.c. of (2) required 13·70 c.c. of iodine, and 100 c.c. of (1) required 28·90 c.c. of iodine; in all, 42·60 c.c., as compared with 42·45 c.c. when mixed, a difference of less than one-third of 1 per cent., which is well within the limits of experimental error.

Properties of the Esters of Phenol and its Homologues.

	Phenyl.	*o*-Tolyl.	*m*-Tolyl.	*p*-Tolyl.
Percentage yield	40·0	48·2	48·3	40·8
B. p./30 mm..................	250°	352°	300°	345°
Sp. gr.	1·621	1·480	1·475	1·495
M. p.	13°	16°	—	14°

The preparation of other esters from the oxides of arsenic and antimony and compounds containing alcoholic hydroxyl is being proceeded with in this laboratory. Attempts are also being made to overcome the difficulties experienced in obtaining the esters of sulphoarsenious acid in sufficient quantities to allow of their compositions being determined.

I wish to express my thanks to Professor W. R. Lang for suggesting this research, and for the interest he has taken in the work.

Chemical Laboratory,
University of Toronto.

ANNUAL GENERAL MEETING,

March 25th, 1909.

Sir William Ramsay, K.C.B., F.R.S., in the Chair.

Dr. G. Barger and Mr. W. B. Tuck were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The President presented the Report of the Council on the progress of the Society during the past twelve months, and the Treasurer, after making a statement as to the Society's income and expenditure for the year 1908, proposed a vote of thanks to the Auditors, which was seconded by Dr. H. G. Colman and acknowledged by Dr. A. Harden and Dr. V. H. Veley.

The adoption of the Report of Council together with the Balance Sheet and Statements of Accounts for the year ended 31st December, 1908, was proposed by Prof. J. Norman Collie, and seconded by Mr. John Spiller. After some remarks by Dr. E. Divers, the motion was put to the Meeting and carried unanimously.

Report of the Council.

The Council once more have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On the 31st December, 1907, the number of Fellows was 2,896. During 1908, 159 Fellows were elected, and 4 were reinstated, thus making a gross total of 3,059. The Society has lost 31 Fellows by death; 38 have resigned; 2 elections have become void, and the names of 38 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1908, was 2,950, showing an increase of 54 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:

J. H. Ball (1902).
S. Banner (1888).
B. H. Brough (1884).
J. T. Cart (1907).
A. V. Cunnington (1898).
A. Deck (1874).
Sir J. Evans (1876).
E. A. Fasnacht (1902).
R. J. Friswell (1871).
Sir J. C. Gamble (1876).
T. A. Gerard (1904).
W. M. Habirshaw (1874).
R. H. Harland (1876).
F. W. Hart (1869).
A. Helms (1894).
A. Houldershaw (1901).
R. V. Jackson (1881).
J. G. Johnson (1872).
W. H. Jowett (1891).
F. H. Leeds (1891).
T. Morson (1851).
H. L. Pendlebury (1907).
J. H. Player (1860).
W. A. Shenstone (1876).
A. Sibson (1859).
F. G. Smith (1903).
E. Sonstadt (1874).
Sir T. Stevenson (1864).
B. H. Thwaite (1880).
A. Wade (1908).
T. H. Walker (1879).

The following Fellows have resigned:

J. Alexander.
J. A. Basker.
F. W. Bayly.
J. H. Belcher.
L. H. Berry.
W. R. Cooper.
A. J. Cownley.
D. C. Crichton.
C. Crocker.
F. W. Daw.
F. A. Drake.
L. Dufty.
G. C. Fry.
T. Gough.
A. H. Green.
H. L. Greville.
E. G. Guest.
C. G. Kiddell.
W. J. Lockyer.
J. Marsh.
L. W. Mathieson.
E. W. Millar.
E. Morris.
W. D. Page.
H. Ross.
H. Rostron.
H. Senier.
F. Shedden.
E. C. Sherwood.
E. S. Smith.
W. Southworth.
A. Turner.
G. J. Ward.
R. Waterhouse.
T. Whittaker.
W. H. Wood.
J. W. Yates.

and Professor A. Haller, whose name has been transferred from the list of Ordinary Fellows to that of the Honorary and Foreign Members.

The number of those Fellows elected prior to 1860 has been diminished by the death of Mr. Thomas Morson, elected on December 15th, 1851, and of Mr. Alfred Sibson, who was elected on December 15th, 1859.

The Council have great pleasure in congratulating Professor William Odling and Mr. E. A. Pontifex on having reached the 60th Anniversary of their Election as Fellows of the Society; the following Fellows during the past two or three years have reached their Jubilee as Fellows:

Prof. A. H. Church (1856).
Sir W. Crookes (1857).
Mr. E. Davies (1858).
Mr. J. F. Davis (1857).
Prof. G. Carey Foster (1856).
Mr. C. Hanbury (1857).
Prof. J. W. Mallet (1857).
Mr. F. Norton (1854).
Sir H. E. Roscoe (1855).
Mr. P. J. Worsley (1858).

The number of Honorary and Foreign Members at the close of 1907 was 29. Seven were elected in February, 1908, but during the past year the Society has had to mourn the death of Professor A. H. Becquerel and of Professor Wolcott Gibbs, thus making the total of Honorary and Foreign Members, at the close of 1908, to be 34. Since then, however, Professor Emil Erlenmeyer and Professor Julius Thomsen, F.R.S., have passed away. Arrangements are being made for the preparation of Memorial Lectures, and that dealing with the life work of Professor Wolcott Gibbs will be delivered by Dr. Frank Wigglesworth Clarke early in June.

A general scheme of co-operation with the Royal Society in the matter of Obituary Notices has been formulated; it will now be possible to issue those relating to deceased Fellows in the publications of both Societies, subject to the consent of the author.

During the year 1908, 278 scientific communications have been made to the Society, 212 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1908 contains 2,281 pages, of which 2,188 are occupied by 222 memoirs, the remaining 93 pages being devoted to the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 205 memoirs, which occupy 2,021 pages.

The Journal for 1908 contains also 4,978 abstracts of papers published mainly in foreign journals, which extend to 2,112 pages, whilst the abstracts for 1907 numbered 4,686, and occupied 2,100 pages. The abstracts for 1908 may be classified as follows :—

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	1,032	1,879
PART II.		
General and Physical Chemistry		936
Inorganic Chemistry		588
Mineralogical Chemistry		97
Physiological Chemistry		567
Chemistry of Vegetable Physiology and Agriculture		265
Analytical Chemistry		646
	1,080	3,099
Total in Parts I. and II.	2,112	4,978

In July, 1908, the Linnean Society celebrated the fiftieth anniversary of the presentation, by C. R. Darwin and A. R. Wallace, of the essay entitled "On the tendency of species to form varieties, and on the perpetuation of varieties and species by natural means of selection"; on this occasion the Chemical Society was represented by the Foreign Secretary, Dr. Horace T. Brown. Another jubilee of especial interest, held in October, was that of the Foundation of the Oxford University Museum, which followed upon the establishment of a Natural Science School at Oxford; at this ceremony the President, Sir William Ramsay, offered to the University the congratulations of the Society.

Late in 1907, the President was nominated on the deputation organised by the British Science Guild, which subsequently represented to the Postmaster-General the desirability of reducing postage rates for the publications of learned Societies; this deputation was received by the Postmaster-General on March 12th, 1908, but his reply was not sympathetic. Following this action, a memorandum on the subject was prepared, and forwarded to certain members of Parliament, some of whom communicated in the matter with the official representatives of the Post Office in the House; the majority of these members, however, were of opinion that it is undesirable to raise this question again at present.

The Society has become indebted to Professor J. Emerson Reynolds for a bust of Michael Faraday.

In May, 1908, a petition, signed by more than three hundred

Fellows, was presented to the Council requesting them to ascertain the wishes of the Society as a whole regarding the admission of women to the Fellowship of the Society. Acceding to the request of the memorialists, the Council directed the Secretaries to issue a letter, drawn up by the Council, in which arguments on both sides were set forth, requesting each Fellow to consider these, and to express his opinion on the ballot paper enclosed therewith. The referendum having closed on October 1st, the scrutators reported that 1,758 voting papers had been received, of which 1,094 were in favour of admitting women, and 642 against the proposal, whilst 22 were neutral. Two Extraordinary Meetings of Council were devoted solely to the consideration of this result, and it was resolved, by a considerable majority, "That in the opinion of this Council it is desirable that at any time, on recommendation of three Fellows of the Society, women be accepted as Subscribers to the Society. Such women Subscribers shall pay an annual fee of thirty shillings: they shall be admitted to all ordinary meetings of the Society: they shall have the same use of the Library as the Fellows, and they shall be supplied with the Proceedings, Transactions, and Annual Reports of the Society as these are issued." The considerations which led the Council to adopt this course are set forth in the statement drawn up by the Council and made by the President at the Ordinary Scientific Meeting on December 17th, 1908 (*Proceedings*, 1908, **24**, 277).

The validity of this resolution having been called in question (*Proceedings*, 1909, **25**, 1), the terms of the resolution and of the criticisms thereon were referred to the legal advisers of the Society, Messrs. Bristows, Cooke and Carpmael, who report as follows:

"In our opinion, the Council had power to pass this resolution. The privileges thereby proposed to be given do not in any way make women subscribers Corporators, and it was because if women were elected Fellows they would become Corporators, that Counsel, in April, 1904, advised they should not be elected Fellows.

"(1) So far as we are aware (taking the parts of the Resolution one by one), there is nothing to prevent women subscribing an annual fee to the Society, or to prevent the Society accepting such fee. Gifts are from time to time made to the Society. The Charter provides that the Council shall have the sole management of the income and Funds of the Society.

"(2) The Resolution also provides that women shall be admitted to all ordinary meetings of the Society. We understand that this has always been the custom.

"(3) The Resolution next provides that the women shall have the same use of the Library as the Fellows. So far as we are aware, there is nothing in the Charter or By-Laws to prevent this, but if it is proposed that the books shall be allowed to circulate among the women Subscribers, then we think that By-Law 15 would have to be altered.

"(4) Lastly, the Resolution provides that women subscribers shall be supplied with the Proceedings, Transactions, and Annual Reports of the Society as these are issued. We see nothing contrary to the Charter or By-Laws in this, and, further, we understand that any member of the public at present has this facility at prices fixed by the Council."

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Professor Frederic Stanley Kipping, F.R.S. The medal will be presented at the Annual General Meeting on March 25th, 1909.

The Council have regretfully accepted the resignation of Mrs. Dougal. A special vote of thanks has been accorded to Mrs. Dougal in recognition of the valuable assistance which she has rendered to the Society during the past fifteen years in indexing its Publications. Dr. C. H. Desch having resigned the position of Assistant Sub-Editor, an arrangement has been made by which all branches of the editorial work will become concentrated in the hands of Dr. Cain and Mr. Greenaway.

Following the important gift of books by Sir Henry Roscoe mentioned in the Report of the Council for 1906, the munificence of the same donor has enriched the Library with a series of periodicals comprising 636 volumes. The Society is indebted also to Mrs. Sonstadt, Mr. Edward Davies, and Professor W. R. E. Hodgkinson, for the gift of valuable sets of books.

The number of books borrowed from the Library during 1908 was 1,339 as against 1,317 in the previous year. The additions to the Library, excluding those already mentioned, comprise 159 books, of which 90 were presented, 412 volumes of periodicals (representing 245 journals), and 36 pamphlets, as against 138 books, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets last year.

In further response to the appeal of the Council referred to in the Report of last year, several Fellows have presented volumes of periodicals to help to complete the sets in the Library. The appeal has also stimulated Fellows to present to the Library a number of early chemical works. The Council welcome gifts of this description, as, in the words of Professor Emerson Reynolds, speaking from the Presidential Chair in 1902, "it is desirable that the Society should have in the Library one copy, at least, of every work printed in English on chemical subjects to the end of the eighteenth century." Each of these gifts has been acknowledged in the Proceedings from time to time.

In consequence of the crowded condition of the Library, it has been again found necessary to construct ten bookcases in the basement; this extension, however, can afford only temporary relief.

The annual income of the Research Fund now amounts to about £346, and this year, as a fair balance was also in hand, grants amounting to £368 were made. In the Transactions for 1908, there are 31 papers contributed by authors who have received grants from the Research Fund.

With regard to the income and expenditure of the Society for the year just closed, there is but little calling for special comment, as both are on the same lines as those of last year. The total income for 1908 is £7,134 17*s.* 2*d.*, which is less than that of the previous year by £125 7*s.* 8*d.*; the expenditure is £6,834 15*s.*, or only £84 6*s.* 7*d.* more than that of last year. This leaves an excess of £300 2*s.* 2*d.* of income over expenditure for the year's working, as compared with £509 16*s.* 5*d.* for 1907, and £741 13*s.* 2*d.* for 1906. It may seem somewhat remarkable that, with an increase of 50 in our list of Fellows, we should have a smaller income from admission fees and from annual subscriptions, which are the items in which there is the most notable falling off. This is, however, accounted for by the large number elected in November and December, whose subscriptions and admission fees do not become due until January 1st, 1909, and therefore do not appear as arrears in the 1908 account, but will swell the income for 1909. This will be welcome to the Treasurer, for the preparation for Vol. V. of the Decennial Index (which has even now begun) must be actively proceeded with by our Editor under the arrangements just concluded. The *Journal* has cost £192 2*s.* 6*d.* more than last year, but a saving of £37 15*s.* 6*d.* has been effected on the *Proceedings.* Administrative expenses are £54 5*s.* 4*d.* less than last year, due to our economies in several directions being greater than increased expenditure in others, but the total effect has been to secure greater efficiency. It is obvious, however, that unless authors will actively aid the Publication Committee in their endeavours to keep down the continual increase in the cost of the *Journal*, it will be necessary to raise the annual subscription from £2 (which it has been ever since the foundation of the Society) to £2 10*s.*

INCOME AND EXPENDITURE ACCOUNT

Income.

		£	s.	d.	£	s.	d.
To Life Compositions					300	0	0
,, Admission Fees					528	0	0
,, Annual Subscriptions—							
Received in advance, on account of 1908		227	0	0			
,, during 1908 ,, 1908		4046	0	0			
,, ,, ,, ,, 1907		296	0	0			
,, ,, ,, ,, 1906		8	0	0			
,, ,, ,, ,, 1905		2	0	0			
		4579	0	0			
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		280	0	0			
		4299	0	0			
Add Arrears at date: 1908 £468; 1907 £18; 1906 £2, estimated to realise as per Balance Sheet		330	0	0			
					4629	0	0
,, Investments:—							
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock		223	15	8			
,, £1050 London and North Western Railway 3 per cent. Debenture Stock		29	18	6			
,, £1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock		43	6	8			
,, £1400 India 2½ per cent. Stock		33	5	0			
,, £2400 Bristol Corporation 2½ per cent. Debenture Stock		57	0	0			
,, £4341 Midland Railway 2½ per cent. Preference Stock		103	2	0			
,, £1200 Leeds Corporation 3 per cent. Stock		34	4	0			
,, £1500 Transvaal 3 per cent. Guaranteed Stock		42	15	0			
,, £1200 North British Railway 3 per cent. Debenture Stock		34	4	0			
Income Tax Recovered		30	14	10			
Interest on Deposit Account		11	9	8			
					643	15	4
,, Publications:—							
Sales:							
Journals		836	4	3			
Proceedings		35	15	6			
General Index		34	9	3			
Memorial Lectures		8	0	1			
Library Catalogue		1	19	6			
Atomic Weight Tables			5	10			
Annual Reports on the Progress of Chemistry		132	6	0			
Jubilee Volume			5	6			
		1049	5	11			
Less Publishers' Commission		100	15	4			
		948	10	7			
Proceeds of Advertisements in Journal	£77 16 3						
Less Commission	11 13 6						
		66	2	9			
					1014	13	4
,, Subscriptions from other Societies:—							
Society of Chemical Industry		8	8	0			
Society of Public Analysts		11	0	6			
					19	8	6
					£7134	17	2

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

11*th March* 1909.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1908.

Expenditure.

		£ s. d.	£ s. d.
By Expenses on account of Journal and Proceedings :—			
Salary of Editor		300 0 0	
Salary of Sub-Editor		200 0 0	
Salary of Assistant Sub-Editor		60 0 0	
Salary of Indexer and Assistance		109 10 0	
Editorial Postages, &c.		23 15 0	
Abstractors' Fees		503 16 3	
Printing of Journal	2568 7 6		
Banding	53 16 9		
		2622 4 3	
Printing of Advertisements		32 5 6	
Wrappers and Addressing		113 12 2	
Distribution of Journal		507 3 6	
Authors' Copies		147 3 0	
Insurance of Stock at Clay's		9 2 2	
			4628 11 10
Printing of Proceedings	197 9 9		
Banding	6 8 6		
		203 18 3	
Distribution of Proceedings		33 17 9	
			237 16 0
,, Preparation for Decennial Index, Vol. V.			30 0 0
,, Annual Reports on the Progress of Chemistry			519 15 9
,, Purchase of back numbers of Journal			15 8 0
,, List of Fellows			60 12 8
,, Library Expenses :—			
Salary of Librarian		130 0 0	
Books and Periodicals		202 11 6	
Binding		49 6 0	
			381 17 6
,, Indexing for International Catalogue			30 0 0
,, Subscription to the Lothar Meyer Memorial Fund			10 0 0
,, Administrative Expenses :—			
Salary of Assistant Secretary		250 0 0	
Salary of Office Assistant		36 10 0	
Wages (Commissionaire, Housekeeper, and Charwoman)		152 19 0	
Pension, Mrs. Hall		30 0 0	
Coal and Lighting		34 7 11	
House Expenses and Repairs		103 12 4	
Tea Expenses		27 7 4	
Insurances		10 8 8	
Accountants' Charges		10 10 0	
Accountants' Commission on Recovery of Income Tax		1 10 9	
Printing		98 3 10	
Stationery		27 8 7	
Postages		103 5 6	
Furniture		12 12 8	
Miscellaneous Expenses		21 16 8	
			920 13 3
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet			300 2 2
			£7134 17 2

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— ARTHUR HARDEN
J. AUGUSTUS VOELCKER,
VICTOR H. VELEY.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31st December, 1908.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance				255	0	0
,, Cash received on Account of Annual Report, Vol. V. (not published)				27	15	6
,, Sundry Creditors				1081	0	9
,, Research Fund :—						
As per last Balance Sheet	10530	17	0			
Less Excess of Expenditure over Income for the year	20	4	7			
				10510	12	5
				11824	8	8
,, Chemical Society : Excess of Assets over Liabilities :—						
As per last Balance Sheet...	19645	9	8			
Add Excess of Income over Expenditure for the year	300	2	2			
				19945	11	10
				£31770	0	6

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2¾ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock... ...	1460	13	6			
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0			
				20297	11	5
(Estimated present value of Investments, £18462 9s. 3d.)						
,, Library, Furniture, Stock of Publications, &c. (not valued)						
,, Sundry Debtors :—						
Society of Public Analysts	11	0	6			
Advertising Agents	66	2	9			
Messrs. Gurney & Jackson	412	8	10			
Telephone Deposit	1	0	0			
				490	12	1
,, Subscriptions in Arrear, £488. Estimated to realise ..				330	0	0
,, Insurance paid in advance				10	5	7
,, Cash at Bank	113	3	0			
,, ,, in hand	17	16	0			
				130	19	0
,, Research Fund :—						
Investments (value when acquired):						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
£1142 16s. New South Wales 3 per cent. Stock ...	1000	0	0			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9			
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	0			
£806 Victoria 3 per cent. Stock	706	6	2			
	10366	17	7			
(Estimated present value of Research Fund Investments, £10070 18s. 11d.)						
,, Cash at Bank	143	14	10			
				10510	12	5
				£31770	0	6

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1908.

Income.

	£	s.	d.	£	s.	d.
To Dividends on :—						
£1000 North British Railway 4 per cent. No. 1 Preference Stock	38	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	146	6	0			
£1034 Great Western Railway 2½ per cent. Debenture Stock	24	11	2			
£1142 16s. New South Wales 3 per cent. Stock	32	11	6			
£1122 Metropolitan Water Board 3 per cent. "B" Stock	31	19	8			
£1365 Midland Railway 2½ per cent. Debenture Stock	32	8	4			
£806 Victoria 3 per cent. Stock	22	19	4			
				328	16	0
,, Repayment of Research Grants :—						
A. E. Dunstan		17	7			
C. E. Fawsitt		7	4			
S. Ruhemann	1	0	4			
W. Barbour	4	13	0			
				6	18	3
,, Income Tax Recovered				12	13	10
,, Balance being Excess of Expenditure over Income Carried to Balance Sheet				20	4	7
				£368	12	8

Expenditure.

	£	s.	d.	£	s.	d.
By Grants to—						
H. Bassett, junr.	18	0	0			
G. D. Bengough	15	0	0			
J. C. Cain	10	0	0			
F. D. Chattaway	15	0	0			
J. A. N. Friend	5	0	0			
N. L. Gebhard	5	0	0			
C. Gilling	20	0	0			
A. G. Green	20	0	0			
P. Haas	7	0	0			
T. P. Hilditch	10	0	0			
Miss A. Homer	5	0	0			
T. M. Lowry	10	0	0			
T. S. Patterson	10	0	0			
F. M. Perkin	8	0	0			
F. G. Pope	5	0	0			
T. S. Price	8	0	0			
S. M. Revington and I. G. Rankin	5	0	0			
J. J. Sudborough	10	0	0			
H. Wren	8	0	0			
G. Young	10	0	0			
R. M. Caven	10	0	0			
A. Clayton	5	0	0			
J. B. Cohen	5	0	0			
C. H. Desch	5	0	0			
A. E. Dunstan	5	0	0			
K. Fisher	7	0	0			
H. B. Hartley	5	0	0			
W. N. Haworth	7	0	0			
G. S. Hibbert	5	0	0			
E. Hope	5	0	0			
A. McKenzie	10	0	0			
A. N. Meldrum	7	0	0			
G. T. Morgan	10	0	0			
W. H. Patterson	5	0	0			
R. H. Pickard	15	0	0			
R. Robinson	10	0	0			
J. L. Simonsen	10	0	0			
Miss I. Smedley	10	0	0			
S. Smiles	10	0	0			
R. Storey	5	0	0			
W. B. Tuck	10	0	0			
C. H. Warner	3	0	0			
				368	0	0
,, Commission on Recovery of Income Tax					12	8
				£368	12	8

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. Keen,
Chartered Accountant.

11*th March*, 1909.

Approved— Arthur Harden.
J. Augustus Voelcker.
Victor H. Veley.

Dr. Divers having given due notice that he would move the adoption of the following new Bye-Law :

XIII *bis.—On Ascertaining the Will of the Society by means of Voting Papers.*

> "The President, either on his own motion or on a written requisition by the Council or by fifty Fellows, shall proceed to ascertain the will of the Society as to any suggested change in the Bye-Laws or in the administration of these laws by the Council, by causing to be delivered, along with the Proceedings or separately, a notice to each Fellow of the change proposed, together with a voting paper upon it, to be filled in by the Fellow and returned to the Secretaries not later than a prescribed date. After that date, the results of the voting shall be counted by the Secretaries and two Scrutineers, appointed by the President, and be reported by him to a Council Meeting and to a General Meeting, upon which the Council shall proceed to act in accordance with the majority of votes, as being the expression of the will of the majority,"

the President declared that his duty prevented him from putting the proposition to the Meeting, the suggested Bye-Law being repugnant to the Charter. Dr. Divers then withdrew his Resolution, and gave notice that at a subsequent General Meeting he would propose the Bye-Law so amended that the word "may" replace the word "shall."

The President then presented the Longstaff Medal for 1909 to Professor F. S. Kipping, who responded in terms expressing his appreciation of the honour bestowed upon him.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. L. T. Thorne, seconded by Dr. McGowan, and acknowledged by Prof. H. E. Armstrong.

The President then delivered his address, entitled "Elements and Electrons." Prof. J. J. Dobbie proposed a vote of thanks to the President coupled with the request that he would allow his address to be printed in the Society's Transactions, the motion being seconded by Prof. F. S. Kipping, and acknowledged by the President.

The Scrutators having presented their report, the President declared that the following had been elected as Officers and Council for the ensuing year.

President : Harold B. Dixon, M.A., F.R.S.

Vice-Presidents who have filled the Office of President : H. E.

Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. Campbell Brown, D.Sc., LL.D.; J. Norman Collie, Ph.D., F.R.S.; J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; James Walker, D.Sc., Ph.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc. Ph.D., F.R.S.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Julian L. Baker; George T. Beilby, F.R.S.; William A. Bone, D.Sc., Ph.D., F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; Charles E. Groves, F.R.S.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. R. Le Sueur, D.Sc.; G. T. Morgan, D.Sc.; A. G. Perkin, F.R.S.; A. E. H. Tutton, M.A., D.Sc., F.R.S.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 25th, 1909.

By SIR WILLIAM RAMSAY, K.C.B., F.R.S.

Elements and Electrons.

> "To decompose the metals, to re-form them, and to realise the once absurd notion of transmutation:—these are the problems now given to the chemist for solution."—MICHAEL FARADAY, 1818; Lecture to the City Philosophical Society.

IN my address last year, my thesis was the claims of the electron to be treated as an element. I tried to show that inasmuch as it has been proved that an electron—an atom of negative electricity, as it may be called—has independent existence, and possesses mass, its claims to substantial nature are as great as those of any of the forms of matter which we term elements. It has been proved that cathode-rays are identical with the β-rays of radicactive substances; that from whatever source the β-rays come, they have approximately the same mass, about one-thousandth of that of an atom of hydrogen; and although their mass is apparently dependent on their velocity, yet they may be considered as of the nature of atoms.

I ventured to suggest that when a metallic and a non-metallic atom combine; when, to take a concrete example, sodium is burned in chlorine, with formation of common salt, an electron leaves the atom of sodium, with which it was previously in combination, to form a link or bond between the atom of sodium and the atom of chlorine. The metal sodium, regarded from this point of view, can no longer be termed elementary; it is a compound of sodion—an ion of sodium—with an electron. When common salt is dissolved in water and "ionised," the sodion is comparatively unaffected by the chlorion; it apparently surrounds itself with a number of water-molecules, as does also the chlorion; it exerts its own osmotic pressure, produces its own special depression in the freezing point and rise in the boiling point of the solution; and, in short, behaves as if it were an independent molecule; similarly with the chlorion. According to this suggestion, the real shift of the electron occurs during the reaction between the sodium and the chlorine; the act of solution, of separating the constituents of the molecule of sodium chloride, makes it possible to detect the presence of its two constituents, the sodion and the chlorion.

It is not always, however, that it can be decided which atom loses and which receives an electron. Not all compounds are ionised on solution. And there is evidence which renders it probable that the electron received from the sodium by the chlorine, the "charge" which converts it into a chlorion, is not the only electron with which the chlorine atom is combined. It appears likely that what we term "elementary chlorine" is not merely a compound of two atoms of chlorine with each other, Cl_2, but that each atom of chlorine carries with it no fewer than seven electrons. An ion of chlorine would therefore be a compound of a chlorine atom with eight electrons; one active, having been received from the sodium or other metallic element present in the compound; the other seven, latent, as it were, and not revealing themselves in such a compound as common salt. A molecule of chlorine, Cl_2, may be regarded on this view as $E_6ClEClE_7$ (where E stands for an electron). These "valencies" are manifested in such compounds as perchloric acid. And if it be permitted to indicate the source of the electron by an arrow head, terminating the dash which is our usual symbol for a "bond" or "affinity," then $Na \longrightarrow Cl$ would show that in common salt, when formed from sodium and chlorine, the electron which forms the bond has been derived from the sodium. If, again, Roman numerals be used to indicate "latent bonds," or unused electrons, $Na \longrightarrow Cl^{VII}$ indicates that a chlorion has eight electrons attached to it, of which one has been derived from the metallic constituent of the salt in solution, while seven belong to it as such. I have tried to expound these views in the last edition of "Modern Chemistry," to which those interested in the matter are referred.

The subject of my present address is the hypothesis that the generic difference between elements is due to their gain or loss of electrons; not of such supplementary electrons as convert an element into an ion, but of electrons more closely associated with the atom, constituents of the atom, as it were. I shall not, however, consider the question as to whether matter is composed of electrons. That is a question well worth raising; but it must follow later; it is not germane to my subject. The question before us is whether, to take a concrete example, an atom of sodium, by losing or gaining electrons, remains an atom of sodium; whether the loss or gain of electrons does not cause it to change into some other element or elements. The arguments in support of this hypothesis are partly theoretical and partly experimental. I am not sanguine enough to suppose that they will at once gain the adhesion of chemists; I should, however, be glad if they were to lead to experimental investigation, for their claim to found a theory must, in the long run, depend on their applicability to experimental facts.

1. It has for many years been an axiom in chemistry that the chemical nature of a compound is due chiefly to the number and arrangement of the atoms which form it, and in a less degree to their intrinsic character. This was first specifically stated by Dumas (*Ann. Chim. Phys.*, 1851, [iii], **33**, 179, 259); his words are: "Every chemical compound forms a complete whole. Its chemical nature depends primarily on the arrangement and number of the constituent atoms, and to a less degree on their chemical nature." Innumerable examples of the justice of this statement, applied to ordinary compounds, might be cited. It is, however, equally applicable to ions; that is, to compounds or elements which differ from others only by the gain or loss of one or more electrons. The metal sodium, for example, if regarded as a compound of sodion with an electron, differs conspicuously from the sodion of common salt; no less different, too, is the chlorion in salt from the element chlorine. If such differences can be produced by the transfer—loss or gain—of one electron, it may be taken as probable that even greater differences would be found, were an element to lose a greater number of electrons. It might be expected that its valency would change, and with the valency its physical and chemical properties.

2. It may be objected that such a loss or gain of electrons by an element is wholly hypothetical. Six or seven years ago, that criticism would have been a just one; it is now, I venture to think, out of date. For we are face to face with the fact that certain elements are continuously parting with electrons, and that when they do so, a change of the nature of transmutation has supervened. It is true that the products of the transmutation of uranium, radium, and thorium (actinium, perhaps, may be regarded as still belonging to that class of elements of which the independent existence requires further proof) are first of all obtainable in such infinitesimal amount that their claim to the term element may be questioned; but the undoubted fact that the well-known helium is a product of the "degradation" of radium must be held to be thoroughly established. And in this instance, one certain case of transmutation is sufficient. *Ex uno disce omnes.*

It may, however, be interesting to chemists to reproduce a table, borrowed chiefly from the second edition of Rutherford's *Radioactivity*, p. 406, which shows the properties of the degradation-products of radium. (The table is slightly altered.)

Products from Radium.

Transformation products.		Time to be half transformed.	Rays.	Chemical and physical properties.
Radium ↓		1200 years	α-rays	Like barium, but more electro-negative; sparingly soluble sulphate and carbonate; soluble halides.
Emanation ↓		3·8 days	α-rays	Chemically inert gas; condenses at low temperature; atomic weight 216?.
Radium *A* ↓	Active deposit of rapid change.	3 minutes	α-rays	Behaves as solid; deposited on surface of bodies; concentrated on cathode in electric field. Volatile at about 1000°. Soluble in strong acids.
Radium *B* ↓		21 minutes	No rays	Soluble in strong acids; volatile at 630°. *B* is more volatile than *A* or *C*. Precipitated along with Ba.
Radium *C* ↓		28 minutes	α-, β-, γ-rays	Soluble in strong acids; deposits on copper or nickel.
Radium *D* ↓		About 40 years	No rays	Soluble in strong acids, and volatilised below 1000°. Possibly "radio-lead."
Radium E_1 ↓		6—6·5 days	No rays	Volatile below 1000°. Soluble in hot acetic acid.
Radium E_2 ↓		4·8 days	β- and γ-rays	Volatile at red heat; more electro-negative than E_1.
Radium *F*		143 days	α-rays	Volatile at 1000°; deposited from solution on to bismuth plate. Probably "polonium."

This table of properties, which might be considerably enlarged, may suffice to convey the conviction that these substances are in reality chemical elements, differing in properties; no one of them has probably been seen, except radium *D*, which Mr. Cameron and I were successful in depositing from the emanation at the conical end of a very fine capillary tube. It was a grey, lustrous metal; and when oxygen was admitted, and the tube was heated, the metallic lustre disappeared. I have not had an opportunity yet of repeating the observation, but hope to do so soon. This substance appears to resemble lead in its reactions; it is contained in the lead chloride, separated from radioactive minerals, and can be separated partially from lead by repeated crystallisation of the chloride. There can be no doubt that when larger quantities of radium are available, some of these substances will be characterised by as definite tests as the ordinary metallic elements.

It is known that the changes of radium and of its emanation are accompanied by an enormous evolution of heat. The latest work on the subject, carried out in Prof. Exner's laboratory at Vienna by E. v. Schweidler and V. F. Hess, shows that the heat-evolution per gram of radium is 118 calories per hour. Rutherford has shown that the emanation, with its rapidly decaying products, RdA, RdB, and RdC, in changing to the long-lived RdD, evolves a quantity of heat about three-quarters of that evolved by the radium from which it is derived; and no doubt each of the changes is accompanied by a definite loss of heat. In other words, these are all endothermic bodies. The question has been raised whether other elements than the radioactive ones are similarly spontaneously changing. It appears to have been proved that the discharge of an electroscope by the ordinary metals is due to their containing a trace of radium, or of some other radioactive metal.

3. Some years ago, in conjunction with Dr. Spencer, experiments have been made similar to those well known for zinc; plates of different elements, placed over the plate of an electroscope, were illuminated with a constant source of ultra-violet light. These plates evolved electrons, but at different rates; the more electropositive metals more rapidly than the more electronegative. It has also been shown by Sir J. J. Thomson that potassium parts with electrons; and by Professor Fleming that the liquid alloy of potassium and sodium does so when illuminated. Now we know many compounds which are sensitive to the action of light; the halides of silver, used in photography, are perhaps the most familiar. The halides of silver are formed by an exo- not an endo-thermic reaction; that is, when they decompose, heat is absorbed, not evolved. Their decomposition therefore is accompanied by an absorption of energy, derived from the pulses of ultra-violet light. A similar case of light-induced chemical change is that of the carbon dioxide and water-vapour of the atmosphere, when they are absorbed by plants, and converted, under the influence of solar radiation, into carbohydrates and other complicated molecules. Here again we have an instance of the energy of the light-waves being stored; the change is an endothermic one.

Instances are not wanting, however, of exothermic chemical change being furthered by light. The rate of interaction of hydrogen and chlorine in the dark is exceedingly slow; but under the catalytic stimulus of violet and ultra-violet light, it becomes explosively rapid.

In short, no general rule can be laid down; in some cases endothermic, in others exothermic, changes are expedited by the action of light-waves.

Knowing that the radioactive elements are actually changing into other "elementary" forms of matter with evolution of electrons (as well as sometimes of α-rays), we cannot, I think, avoid the inference that where electrons are evolved, a change from one form of element to another is in progress. If not proved, it is at all events probable. The spontaneous "degradation" of the radioactive elements is an exothermic change; the "degradation" of the other elements under the stimulus of light-waves, judging by the analogy of photo-sensitive compounds, may or may not be accompanied by evolution of energy. Probably in some cases it is; in others it is not.*

4. In his Faraday lecture, Professor Ostwald, in 1904, likened the elements to stalactites hanging from the roof of a cave, some longer, some shorter. The absorption of energy by a long stalactite may serve to shorten it, and to alter its position. But while the commoner elements (and therefore the more stable) are difficult thus to displace, owing to the enormous amount of energy required to effect the displacement, the radioactive elements are, as it were, displacing themselves spontaneously, and losing energy in so doing.

Inasmuch, moreover, as the effect of energy is proportional not merely to its total quantity, but to its intensity, and inasmuch as its intensity is closely related to its concentration, it is to be expected that just as the concentration by Sir Humphry Davy of electric energy into the small area of the ends of two platinum wires enabled him to decompose the alkalis, so a high concentration of energy will effect the change of one element into another, or into several others.

5. Turning next to another line of evidence, let me allude to a paper read to the Society in February last, by my friend, Mr. Alfred Egerton, in which he points out regularities in the irregularly regular series of atomic weights. Attempts to introduce order into this series have generally been made by the device of an arithmetical or geometrical series, from which divergences are represented by arbitrary factors; in short, attempts of this nature introduce arbitrary constants. Mr. Egerton considers the question: Why are the atomic weights of many of the elements multiples of that of oxygen? I must refer those interested in the subject to his paper (Trans., 1909, **95**, 238); I will merely state here that almost absolute coincidence between the best known values of the atomic

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* I may remark here, parenthetically, that it has been suggested that a possible source of energy, available in the future, when our fuel is exhausted, might be derived, if a catalyst for the exothermic change of one form of elementary matter were discovered. The remarks made above point to the conclusion that such a hope is probably destined to be illusory; for the balance of probability is in favour of the elements as we know them being stable bodies; to "degrade" them, as much energy would have to be absorbed as would be given out by a reversible process, and that energy could be obtained only from known sources. For the main supply of energy therefore, we have nothing to look to beyond our coal-mines. At the same time it should be mentioned that Prof. Lenard inclines to the belief that the "degradation" of elements is always exothermic.

weights and his calculated numbers are arrived at on the simple hypothesis that multiples of the mass of a definite number of electrons are added to, or subtracted from, the atomic weight, expressed as a round number. The statement is saved from being arbitrary, inasmuch as the multiple ascends in nearly regular progression. It may almost be said to follow from this view that if electrons could be added to, or subtracted from, the atoms of elements in definite numbers, transmutation would be effected.

So far, I have endeavoured to state the various arguments in favour of the possibility of transmutation. They are, briefly stated:

1. The subtraction from, or addition to, an atom of an element of one or more electrons, by virtue of which it is converted into an ion, completely changes the properties of that element.

2. The fact is incontestably proved that certain elements, termed radioactive, are losing electrons, and are thereby being converted into other forms of matter, which in our present nomenclature have equal claim to be considered elementary.

3. The influence of ultra-violet light on many, if not all, elements is manifested in causing them to part with electrons; it is not, however, thereby proved that they yield other elementary forms of matter.

4. The effect of chemical change is usually manifested in a gain or loss of energy. There is reason to believe that change from one elemental form of matter into another would be accompanied by an unusually large gain or loss of energy, for it is known that the "degradation" of radium is coincident with the loss of a relatively enormous amount of energy. This energy, moreover, is in a highly concentrated form; much energy is contained in small volume, or, what amounts to the same thing, in small mass, using the word in the sense of quantity of matter.

5. It appears that the irregular regularity of the numbers representing the atomic weights can be represented on the hypothesis that the addition or subtraction of definite groups of electrons is the cause of their divergence from a perfectly regular series.

These arguments, however, can be regarded only as furnishing strong ground for experimental investigation; and I propose in the rest of my address to give a brief sketch of what has been attempted. No one is better aware than I am how careful one should be in publishing results; but it has appeared to me best to make public the conclusions to which my experiments have led me; if the experiments are faulty, they will be repeated and corrected; if just, they will be corroborated.

I need here only allude to the transformation of radium emanation into helium, discovered by Mr. Soddy and myself. The accuracy of this observation has been amply established. Owing to the fact that during this transformation the energy evolved is in the most concentrated form known, and that the emanation of radium is fairly easily soluble in water, and therefore in aqueous solutions, the action of the emanation on a solution of copper sulphate and nitrate was investigated, glass vessels being employed. Four experiments were made, each one in duplicate; the duplicate was in each case treated like the solution containing emanation; the only difference was that the duplicate-solutions contained no emanation. From the emanation-solutions, a larger residue was obtained in each case than from the duplicate; and while the residue from the emanation-solutions showed the presence of a trace of lithium, those from the duplicates failed to give spectroscopic evidence of the presence of lithium. The fact of the experiments having thus been carried out in duplicate renders inapplicable the criticism of Professor Hartley, that inasmuch as lithium is a widely distributed element, accidental contamination is probable. But the alleged repetition of the experiments of Madame Curie and Mlle. Gleditsch, in which, using platinum vessels, they obtained no greater residue, and no trace of lithium, cannot be thus explained away. There are two possible replies: either the conditions of experiment varied, so that the same result was not obtained; or it is conceivable that in presence of emanation and a copper solution, a trace of lithium was dissolved from the glass vessel (which had been tested for lithium, however, with negative result), which escaped solution in absence of emanation, on the one hand, or in absence of copper, on the other. For emanation in presence of distilled water in a vessel of the same glass gave a minute residue in which the spectrum of lithium was not to be observed.

I may be permitted here to mention a research carried out by Mr. Alexander Cameron, under my supervision, on the action of emanation on a solution of silver nitrate in a silica bulb, no glass, but only silica and platinum vessels, having been used for the experiments. Two experiments were made, in which the silver nitrate solution was left for a month in presence of the emanation from 0·2111 gram of radium, reckoned as metallic. Two similar blank experiments were made, in which no emanation was introduced into the bulb. These experiments had the object of ascertaining whether the "treated" silver nitrate gave a larger residue than the "untreated." The utmost pains were taken, it is needless to say, to avoid the introduction of any solid matter with the reagents employed. The results were negative; they are as follows:

	Residue from "treated" silver nitrate.	Residue from "untreated" silver nitrate.
Expt. 1	0·00022	0·00032
,, 2	0·00027	0·00007

The differences are so small, and the difficulty of avoiding contamination so great, that no positive conclusion can be drawn from the experiments. It is really impossible to manipulate quantities of the order of a few tenths of a milligram. The residues showed only the spectrum of sodium.

But the available energy of the radium emanation was certainly largely expended in producing another change, for a large amount of metallic silver was deposited—no less than 0·23 gram. Besides this, the gases evolved consisted of: Oxygen, 1·038 c.c.; hydrogen, 0·071 c.c.; nitrogen, 0·084 c.c.; and carbon dioxide, 0·016 c.c.;* in all, 1·209 c.c.

The total amount of emanation with which these solutions were treated was respectively 0·78 and 0·92 of that evolved from a gram of radium in 3·86 days—a comparatively large dose, and one capable of evolving about 5,000 gram-calories.

It is, however, possible that silver is a very "stable" element, and that a bad selection has been made. Judging again by analogy with compounds, if it were required to separate carbon from one of its compounds, it would puzzle a beginner if carbon dioxide were the particular carbon compound fixed on as a source of carbon; while, with cane-sugar, mere application of heat would reveal its content of carbon. Only repeated experiment can solve this problem—to discover the less stable, and therefore more easily degraded, elements. Probably they should be sought for among those of high atomic weight.

I have, however, stumbled across a case of apparent transformation, in working in a totally different direction. After the demonstration that helium is a transformation-product of radium, Debierne showed that it is also to be obtained from actinium. Naturally, the idea occurred that thorium should also yield helium. Now, the radioactive constant of thorium is only the 1/180,000th part of that of radium; hence the necessity of working with a very much larger quantity, over a very much longer time.

Miss Burke was so good as to purify for me 270 grams of thorium nitrate, $Th(NO_3)_4$. On December 20th, 1905, it was dissolved in about 300 c.c. of water, and introduced into a round-bottomed flask, provided with a capillary neck, on which was sealed an excellent stopcock. The stopcock was greased, and after the flask had been evacuated with a Töpler pump, the tap was closed. After some hours, it was again pumped empty, and again left; and this proceeding was repeated at intervals, until absolutely no gas could be pumped off. The thorium nitrate was fairly acid, for unless some free acid is present, it is difficult to avoid its being hydrolysed by water. After this complete withdrawal of all gas, the glass connexion to the Töpler was broken; the upper part of the capillary tube, above the stopcock, was filled with water, and the flask was inverted into a jar of water. During the three years in which the gaseous contents of the flask were under observation, no trace of leakage at the stopcock occurred; no water entered. Had leakage occurred, it would have been detected by a line of demarcation in the capillary tube, between the strongly refracting solution of thorium nitrate and the less refractive water.

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* The carbon dioxide was probably due to the grease of the stopcock of the burette in which the explosion was carried out.

The flask was left for 168 days, and was then sealed to a Töpler pump, with a U-tube, cooled with liquid air, interposed between the flask and the pump. On opening connexion to the pump, a white substance deposited in the U-tube. As the presence of carbon dioxide was not suspected (the experiment having been made to test for helium), this white deposit was not investigated; there was, however, a suspicion that it might be carbon dioxide. The total volume of gas collected measured 3·523 c.c.; it contained 0·061 c.c. of explosive mixture of hydrogen and oxygen. The residue was mixed with excess of oxygen, and the nitrogen removed by sparking in presence of caustic potash. The gas remaining was then introduced into a tube containing phosphorus, and the oxygen was removed. The minute residue was forced into a minute capillary vacuum-tube, and its spectrum examined. The tube was nearly phosphorescent; I could not be certain, but I suspected that I saw the yellow line of helium. The flask was treated as before, and set aside for 250 days (June 6th, 1906, to February 11th, 1907). The gas then pumped off was analysed. Its volume was 5·750 c.c.; it contained 0·588 c.c. of carbon dioxide, absorbable by potash, and 0·017 c.c. of hydrogen plus oxygen; the residue, 5·145 c.c., was pure nitrogen. Here the volume of gas emitted from the thorium nitrate was nearly proportional to the time. Again, helium was sought for, but without definite result; the yellow line was doubtful.

After closing the flask as before, it was kept for 173 days, until August 3rd, 1907. The gas, on analysis, gave carbon dioxide, 1·08 c.c.; hydrogen and oxygen, 0·02 c.c.; and nitrogen, 1·64 c.c.; the total volume was 2·74 c.c. The testing for helium was very satisfactory as regards manipulation, but the presence of the D_3 line was questionable.

On August 14th, 1907, a control experiment was started, in which a solution of 300 grams of mercuric nitrate, in the minimum quantity of water, was enclosed in a similar flask, pumped empty, and inverted. This salt was chosen because mercury is not supposed to be a radioactive metal, and because of the known oxidising qualities of mercuric nitrate. The gas withdrawn from this flask on March 30th, 1908, consisted of 0·015 c.c. of carbon dioxide, 0·034 c.c. of oxygen, and 3·628 c.c. of nitrogen. That from the bulb with thorium nitrate contained 1·209 c.c. of carbon dioxide, 0·016 c.c. of hydrogen and oxygen ($H_2 + O_2$), and it left a residue of 1·321 c.c. of nitrogen. After sparking down, there was distinct evidence of a helium spectrum; that is, the D_3 line was observed, but the tube almost at once "ran out." To make certain, however, of the production of helium from thorium, a larger quantity is evidently necessary.

The next analysis was made on February 9th, 1909. It occurred to me that although the grease on the stopcock had been exposed to only a trace of liquid—that in the narrow capillary tube—still, carbon dioxide might have been produced in presence of thorium, although the similar experiment with mercuric nitrate gave a practically negative result. To guard against this, a little metallic mercury was introduced, without letting in a trace of air. When the flask was inverted, the capillary tube was filled with mercury, which effectually protected the stopcock from contact with the thorium solution. On examining the flask on February 9th, 310 days after the gas had been withdrawn, no bubbles could be detected between the stopcock and the mercury; had carbon dioxide risen from the grease, it must have been trapped there.

The result of the presence of this mercury was unexpected. Instead of 3 or 4 c.c. of gas, no less than 180 c.c. were collected; analysis of a small portion showed that it was almost pure nitrogen. To extract the carbon dioxide, the whole of this gas was liquefied in a bulb cooled with liquid air, under a pressure of two atmospheres; and the nitrogen was allowed to boil away into a gas-holder. The residue in the bulb was collected separately. The process was repeated a second time. The first small portion of gas contained 0·411 c.c. of carbon dioxide; the second, 0·103, in all 0·622 c.c. It is probable, however, that not all was then separated, for carbon dioxide has still a small vapour pressure at −185°.

These experiments render it at least probable that thorium nitrate "engenders" carbon dioxide; or, in other words, that one of the degradation products of thorium is carbon.

To test this question further, two quantities of thorium nitrate, carefully purified, were treated with radium-emanation, which had stood for some hours in a tube containing moist potash. It was introduced rapidly into a bulb, and the only chance of contamination with carbon compounds was while it passed through a stopcock on its way to the bulb; the time of contact cannot have been a fraction of a second. A special experiment, to be described elsewhere, has shown that grease, in contact with emanation, yields, when oxygen is absent, nothing but pure hydrogen; not a trace of carbon dioxide.

The first quantity of thorium solution was charged with emanation on June 3rd, 1908; the bulb was opened, and the gas analysed, on November 18th. Nitric peroxide was present; it was removed by shaking with mercury, some pure oxygen having been added to combine with nitric oxide. The volume of the gas was then 5·579 c.c. No electrolytic gas was present, but 0·551 c.c. of carbon dioxide, 1·342 c.c. of oxygen, and 3·686 c.c. of nitrogen. The method of filling this bulb absolutely precluded entry of air at any time. The same solution in the same bulb was recharged with a much smaller quantity of emanation on November 20th; the bulb was opened on February 2nd, 1909. After removal of oxides of nitrogen with mercury as before, the volume was 1·789 c.c.; it contained 0·124 c.c. of carbon dioxide, 1·026 c.c. of oxygen, and 0·639 c.c. of nitrogen; there was no electrolytic gas.

From these experiments it would appear that the action of radium emanation on thorium nitrate solutions is also attended with the formation of carbon dioxide. Thorium belongs to the same natural family as carbon; and experiments were next tried with another member of the same family, namely, zirconium. Two bulbs were therefore charged with an acid solution of zirconium nitrate, and each "dosed," on August 19th and 26th, 1908, respectively, with the radium emanation from 0·2111 gram of radium as bromide, gathered during eight days. The gases were analysed as on the 20th November. After oxides of nitrogen had been removed, the remaining samples had the following composition:

	I.	II.
Carbon dioxide	0·124	0·116
,, monoxide	0·002	0·008
Nitrogen	0·456	0·762
Oxygen........................	3·831	3·665

There was no electrolytic gas.

Having obtained carbon dioxide from zirconium nitrate, hydrosilicofluoric acid was similarly treated with the emanation of a week's gathering from the same quantity of radium. The carbon dioxide from 10·2 c.c. of what was practically all electrolytic gas amounted to 0·106 c.c. I am much indebted to Mr. Usher for carrying out the analyses of these gases.

To ascertain whether lead, too, yielded carbon dioxide, a bulb was charged with an acid solution of lead chlorate, and dosed with emanation; the bulb was set aside on December 18th, 1908; the gases were extracted and analysed on January 26th, 1909. The bulb contained a thick deposit of lead peroxide; the gas did not attack mercury, hence there was no free chlorine; it consisted wholly of oxygen, 5·192 c.c., and carbon dioxide, 0·007 c.c. The amount of the latter gas is here insignificant; and the experiment may be regarded as a blank one as regards the production of carbon dioxide.

A similar experiment was made with bismuth perchlorate, obtained by dissolving bismuth oxychloride in excess of perchloric acid, and evaporating until the solution became syrupy, and until white fumes appeared. Some crystals deposited on cooling. The oxychloride was testing for nitrates and nitrites with brucine; none were present. The pressure in the bulb, on opening, was very high, due to formation of oxygen and chlorine. The total amount of carbon dioxide found was 0·150 c.c., and of oxygen about 48 c.c. Now, as the solution of bismuth perchlorate had been evaporated until fumes of perchloric acid were evolved, and as all carbon compounds—dust, etc.—must certainly have been oxidised, the formation of carbon dioxide appears certain. The mercury which had absorbed the chlorine was carefully tested for nitrates and nitrites, but with negative result; and no nitrogen was present in the gases produced. This may appear curious, for bismuth belongs to the nitrogen group; but in such matters it would be bold to predict. The fact that nitrogen was absent from the bulbs containing bismuth and lead points to the absence of air, and inferentially also to its absence in the other experiments described. Indeed, it is certain that in all these experiments all gas was initially extracted from the solutions; and no gas entered during the subsequent manipulations.

Much more might have been said regarding the special precautions taken. For example, a pump with a specially narrow fall-tube was employed; 1 cm. of its length contained about 1 cubic millimetre. The exhaustion of the bulbs was carried so far that no appreciable bubble passed down the fall-tube; 1/100th cubic millimetre could have been easily detected. Again, all vessels were washed out with hydrogen made by heating palladium-hydrogen in connexion with a pump; tubes, explosion-burette, measuring-burette, etc., so as to avoid all posible source of contamination. In short, every precaution which could be thought of was taken to exclude all foreign gases. The emanation, besides, before it was introduced into the bulbs, had stood for several hours over moist potassium hydroxide; that treatment has been found repeatedly to exclude all traces of carbon dioxide, for it has been tested for spectroscopically and its absence conclusively proved.

Such are the facts. No one is better aware than I how insufficient the proof is. Many other experiments must be made before it can confidently be asserted that certain elements, when exposed to "concentrated energy," undergo degradation into carbon.

The nature of the Presidential Address delivered to the Society on the occasion of its Anniversary Meeting has varied with the occupant of the Chair. Up to 1903, the custom has been for the President to adopt the Report of the Council, and to make any remarks on it which he deemed appropriate. In that year, Professor Emerson Reynolds made separate comments on the Report, and added to it certain observations dealing with the progress of chemistry. From the date of my admission to the Society in 1873 up to 1887, when Dr. Hugo Müller occupied the Chair, this was the uniform practice. It was broken by Sir William Crookes in 1888, whose address treated of "Meta-Elements." Professor Armstrong said in 1894: "It should be the duty of the occupant of this Chair to deliver a technical address"; and I hold that he was right. The President of a Society like ours reaches office at an age when he may be expected to have accumulated valuable experience, which it is his privilege to bring to the notice of the Society. And on this conviction I have endeavoured to act.

The history of the Society during the past year has been sufficiently given in the Report of the Council, to which I have nothing to add. I wish, however, in transferring office to my distinguished friend and colleague, Professor Dixon, to express my sense of the great honour which has been bestowed on me in the Presidentship of the Chemical Society; also to express regret for any shortcomings during my tenure of the office; I have endeavoured to do my best to promote the interests of the Society. In this I have to record my indebtedness to the Fellows for their uniformly courteous treatment of "the Chair"; to the Council of the Society for help and support in deliberations at meetings; and in especial degree to the officers of the Society, notably to the Secretaries, with whom the most cordial relations have always subsisted, and whose unfailing help in all matters connected with the Society I have to acknowledge with feelings of the warmest gratitude.

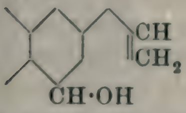
LXXVIII.—*Contributions to the Chemistry of Cholesterol and Coprosterol.*

By Charles Dorée.

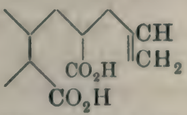
Part I.—*The Presence of a Second Unsaturated Linking in the Cholesterol Molecule.*

Cholesterol, as is well known, behaves chemically as an unsaturated alcohol. It readily forms dihalogen additive products, and thus possesses certainly one double linking in the molecule. In this respect all the isomeric animal and vegetable cholesterols are similar to it (Dorée, *Biochem. J.*, 1909, **4**, 72), and from a physiological point of view the double linking is of importance, since it has been shown that the antitoxic function exerted by the naturally occurring cholesterols towards the hæmolytic action of such poisons as saponin, is reduced to a minimum if the double linking be saturated or modified. The position of this double linking in the molecule has been shown by Windaus (*Ber.*, 1906, **39**, 2008) and by Dorée and Gardner (Trans., 1908, **93**, 1328) to be situated at the end of a side-chain of carbon atoms. In 1907 Windaus (*Ber.*, 1907, **40**, 3681) by the reduction of phytosterol with sodium in amyl-alcoholic solution obtained a dihydrophytosterol, which was, however, still unsaturated towards bromine. It appeared therefore that phytosterol, unlike cholesterol, contained two double linkings, one of which reacted with hydrogen, and the other with bromine. The use of ozone as a reagent for characterising the unsaturated linkings of organic compounds was first demonstrated by Harries (*Annalen*, 1906, **343**, 311), and has recently been especially emphasised by Molinari (*Ber.*, 1907, **40**, 4154; 1908, **41**, 585), who considers the reaction with ozone to be better than any other for this purpose. According to Harries, unsaturated compounds combine with ozone, each double bond becoming saturated by the addition of one molecule of ozone. Compounds such as aldehydes, ketones, and acids, which contain the carbonyl group, further unite with one atom of oxygen at each such grouping, and on treatment with water this is eliminated with the formation of hydrogen peroxide. The latter point, it may be mentioned, is disputed by Molinari, who considers the reactions for hydrogen peroxide obtained by Harries to be due to the presence of aldehydic and other substances.

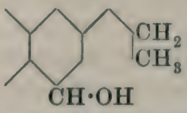
As the result of an examination of the action of ozone on phytosterol, Molinari found both by the determination of the amount of ozone added (the ozone number), and by analyses of the ozonide obtained, that phytosterol forms a compound, $C_{27}H_{46}O{\cdot}O_6$, and therefore contains two unsaturated linkings in the molecule (*Ber.*, 1908, **41**, 2782). Cholesterol and the recently discovered bombicesterol were found to behave similarly towards ozone, and these substances would therefore appear to possess a second and previously unknown double linking in the molecule. That this might be the case had been previously pointed out by the author and J. A. Gardner (*loc. cit.*), who found that the compound obtained by the prolonged action of ozone on cholestenone after repeated purification gave numbers on analysis which corresponded with the formula $C_{27}H_{44}O{\cdot}O_7$, that is, the correct oxygen content for a compound possessing two double bonds and a carbonyl group. Analyses of ozonides dried in a vacuum are for various reasons far from satisfactory. In the simple ozonides analysed by Harries and his co-workers, the carbon percentage is frequently one or more units too low, and in the case of cholesterol derivatives this difficulty would no doubt become still more apparent, since these compounds are notoriously difficult to burn successfully. The determination of the ozone value in the cases examined by Molinari gave far more satisfactory results, but the method is extremely tedious, as the complete removal of the solvent in a vacuum requires from four to seven weeks. Molinari found, however, that the solvent could be most expeditiously removed by heating the ozonides in a vacuum at 60—65°, when, in the case of cholesterol and phytosterol, a constant weight was obtained in half an hour, and the ozonides were found to be stable up to a temperature little short of 100°. It was thought, therefore, to be of interest to ascertain whether this method of studying the action of ozone could be extended to a number of cholesterol derivatives, with the ultimate object of throwing some light on the nature of the second double linking in these substances, and of explaining, if possible, some of the anomalies previously observed in connexion with the behaviour of apparently saturated or unsaturated derivatives of cholesterol towards bromine. For this purpose the action of ozone on the following compounds was examined. The schematic formulæ given have no great value, but represent the opinion at present held as to the structure of that part of the molecule of cholesterol which includes the first double linking, and illustrate the supposed relationship of the other derivatives to the mother substance:



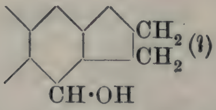
I. Cholesterol, $C_{27}H_{46}O$.



II. Acid, $C_{27}H_{44}O_4$.



III. β-Cholestanol, $C_{27}H_{48}O$.



IV. α-Cholestanol, $C_{27}H_{46}O$.

(V) Coprosterol, $C_{27}H_{48}O$, and (VI) ψ-coprosterol, the relationships of which to cholesterol and to one another are unknown: the ketones corresponding with these alcohols, namely, (VII) cholestenone, $C_{27}H_{44}O$, (VIII) β-cholestanone, $C_{27}H_{46}O$, and (IX) coprostanone, $C_{27}H_{46}O$, the ketone given both by coprosterol and ψ-coprosterol.

EXPERIMENTAL.

The ozone used in these experiments was prepared as follows: Oxygen from a cylinder was passed through concentrated sulphuric acid, and then through an ordinary tube ozoniser. A large spark coil was employed, which, when working steadily, required 1·5 to 2 amperes at 4 volts. The ozonised oxygen, without any after treatment, was passed first through an empty flask, and then through absorption bottles containing the solutions to be ozonised. The solvent used throughout was purified chloroform. The ozonised gas was passed at the rate of from 5½ to 6 litres per hour, and was found to contain almost exactly one per cent. of its weight of ozone.* The solutions were not specially cooled, but the experiments were carried out in a very subdued light. In some cases, the chloroform was evaporated off in the ozone stream as recommended by Molinari; but in others this was found to be unsatisfactory. When saturated with ozone, the liquid was brought into a small, weighed distillation flask, the solvent distilled off in a vacuum, and the ozonide heated on a water-bath kept at a constant temperature, a high vacuum being maintained throughout. The flask was weighed at frequent intervals until no further loss occurred.

Experiments with the Acid, $C_{27}H_{44}O_4$.

This acid was prepared by the oxidation of cholesterol with potassium hypobromite (Diels and Abderhalden, *Ber.*, 1906, **36**, 3177). Its reactions, and especially its behaviour on oxidation, make it very probable that it is formed by the conversion of the $CH_2{\cdot}CH{\cdot}OH$ group of cholesterol into two carboxylic groups with opening of the ring. It would, therefore, still contain the unsaturated side-chain of cholesterol, but in spite of this it is quite indifferent to bromine. The acid is almost completely insoluble in all the usual solvents with the exception of glacial acetic acid, from which it was obtained in prisms melting at 290°. A quantity of the finely-powdered substance was suspended in chloroform, and submitted to the action of the ozonised oxygen. In a few hours the solution became perfectly clear, and it was apparent that a soluble ozonide had been formed. This clearing of the suspension marks a stage in the action of the ozone which was explained by the following results:

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* Estimated by absorption of the ozone in a weighed quantity of olein (Molinari).

(*a*) 0·9616 gram of the acid suspended in chloroform was treated with ozone until the whole of the substance had passed into solution. After evaporation of the solvent the pure white foam remaining was heated in a vacuum at 60°, and after one and a-half hours attained a constant weight. This weight was not altered after a further one hour at 60°, and one week in a vacuum:

0·9616 added 0·1018 O_2. Oxygen = 10·6.

$C_{27}H_{44}O_4 \cdot O_3$ requires added oxygen = 11·1 per cent.

This ozonide was a light, white, friable substance.

(*b*) In this case the acid was treated as before, the action being stopped as soon as the solution had become clear, but the solvent was removed by heating at 38° in a vacuum. At this temperature the weight diminished extremely slowly. At the end of one week's heating the increase of weight was 16·3 per cent.; at the end of the next it had become 14·4 per cent. In three weeks the increase still amounted to 13 per cent., and in four weeks to 12·2 per cent.; after the end of the fifth week, no further loss occurred, and the weight became constant as follows:

0·7026 added 0·0800 O_2. Oxygen = 11·4.

$C_{27}H_{44}O_4 \cdot O_3$ requires added oxygen = 11·1 per cent.

(*c*) The first effect of ozone on this acid, therefore, is to saturate one double linking, and in order to ascertain, if possible, whether this double linking was the one situated in the side-chain of the original cholesterol molecule, which should still be present in the acid, the action of water on the ozonide was studied. The ozonide was mixed with gas-free distilled water, and heated on a water-bath, while a slow current of air, purified by passage through a series of potash bulbs, was passed through the apparatus. The gases evolved were led into a receiver, and then passed through a solution of baryta. An evolution of carbon dioxide was at once apparent, and a slow and steady decomposition of the ozonide took place, a considerable quantity of barium carbonate being ultimately produced. As previous experience with the ozonide of cholestenone had shown that the evolution of the carbon dioxide was not quantitative, no attempt was made to estimate the amount evolved in this case, but its recognition as one of the products of decomposition of the ozonide, $C_{27}H_{44}O_4\cdot O_3$, shows that the ozone is attached at a terminal pair of carbon atoms. Harries has shown that on treatment of the ozonides of unsaturated compounds with water, rupture of the carbon chain takes place at the position of the double bond, with the formation of aldehydes or ketones and hydrogen peroxide, which frequently produce a further oxidation, as in this case.

(*d*) In the next experiment, the prolonged action of ozone on the acid was examined. 0·9578 gram was treated for eighty hours with the ozonised gas, the chloroform being replaced as it evaporated. After a long time the clear solution began to appear turbid, a gelatinous skin formed on the surface, and drops of clear jelly were deposited on the sides. As it was not possible to remove these from the absorption bottle, the chloroform was distilled off, and the bottle and its contents heated at 65° in a vacuum. The loss of weight was very slow, but after ten hours became constant. The weight remained unaltered after a further period of two hours at 70°:

0·9578 added 0·2432 O_2. Oxygen = 25·4.

$C_{27}H_{44}O_4\cdot O_6$ requires added oxygen = 22·2; $C_{27}H_{44}O_4\cdot O_7$ requires 25·9; $C_{27}H_{44}O_4\cdot O_8$ requires 29·6 per cent.

In the case of this acid, with two double linkings and two carbonyl groups, an addition of eight atoms of oxygen might be expected. The value found points rather to the addition of seven.

The ozonide obtained in this experiment was a slightly brown, friable solid; in places where it had adhered to the vessel it appeared as a clear pale-brown glass. It was sparingly soluble in chloroform or benzene, but readily so in acetone. On treatment with water, carbon dioxide was evolved. During the heating with water, the fragrant odour previously noted with the ozonides of cholesterol and its derivatives (Trans., 1908, **93**, 1328) was again observed. It was also apparent in a less degree during the evaporation of the solvent, but diminished as the weight approximated to a constant quantity.

(*e*) In this experiment, 0·7401 gram of the acid was ozonised as before. In six hours the solution had become clear, and the ozone stream was passed for 100 hours more. During the last few hours the white, gelatinous substance began to appear, and the action was then terminated. After removal of the solvent, the ozonide, which was pale brown, was placed in the dark in a vacuum at 38°. In twenty-four hours it had become distinctly brown, but no deepening of the colour was apparent during the next month. At the end of this time its weight had become constant, no appreciable loss occurring during the next eighteen days:

0·7401 added 0·2412 O_2. Oxygen = 32·5.

$C_{27}H_{44}O_4 \cdot O_8$ requires added oxygen = 29·6 per cent.

As the result of these experiments, it would appear that the ozone attaches itself first to the reactive double linking of the side-chain, and that subsequently and very slowly addition of a molecule of ozone takes place at a second double linking, the position of which is unknown, with probably simultaneous addition of oxygen to the carbonyl groups.

Experiments with Cholestenone.

The ozonide of this ketone has already been investigated (Trans., 1908, **93**, 1328). By prolonged ozonisation, purification by solution in ethyl acetate, and precipitation with light petroleum, a product was obtained which gave, on analysis, figures corresponding with the formula $C_{27}H_{44}O \cdot O_7$, and pointing to the presence of two double linkings in the cholestenone molecule. The following experiments were now carried out:

(*a*) 1·0133 grams of cholestenone (m. p. 81°) were ozonised for eighty hours, a perfectly clear solution being obtained. The resulting ozonide was a pure white foam, and was heated in a vacuum at 45—50°. After ten hours the weight became constant. The odour of orange oil, which was at first very prominent, gradually disappeared with the elimination of the solvent:

1·0133 added 0·2905 O_2. Oxygen = 28·67.

$C_{27}H_{44}O \cdot O_7$ requires added oxygen = 29·2 per cent.

In appearance and properties, as well as in composition, this ozonide exactly resembled the one obtained as previously described.

(*b*) 0·7350 gram of cholestenone was ozonised as in the preceding experiment, and for the same length of time, but after removal of the bulk of the solvent the ozonide was at once heated to 70°. After two hours the increase of weight amounted to 23 per cent., and the ozonide appeared as a glassy, brown substance, filled with gas bubbles. In four hours more, the increase in weight was still 20 per cent. The flask was then heated to 80°, and in six hours lost a further 6 milligrams, the weight then becoming constant:

0·7350 added 0·1187 O_2. Oxygen = 16·15.

$C_{27}H_{44}O \cdot O_4$ requires added oxygen = 16·7 per cent.

The ozonide was now a smooth, brown, transparent glass. It was heated for two hours more at 80°, and half-an-hour at 90°, without alteration in weight. On boiling for six hours with water in a stream of air, as previously described, a large quantity of carbon dioxide was evolved, and the bulk of the solid residue was found to be insoluble in light petroleum, no doubt consisting, as previously shown, of the acid $C_{26}H_{42}O_3$.

These results confirm those already described as a result of the study of the acid $C_{27}H_{44}O_4$. In this case we have the ozonide $C_{27}H_{44}O\cdot O_7$, stable at a low temperature, but decomposing on heating to the ozonide $C_{27}H_{44}O\cdot O_3$, in which the oxygen is attached to the reactive double linking of the side-chain.

β-Cholestanol, $C_{27}H_{48}O$.

A method for the preparation of this substance has recently been given by Willstätter and Mayer (*Ber.*, 1908, **41**, 544), which leaves little doubt that it is the dihydrocholesterol corresponding with cholesterol dibromide (Formula III). The method consists in the direct reduction of cholesterol by hydrogen in the presence of platinum black. After some difficulty, a considerable quantity of the substance was prepared in this way. The substance did not decolorise a solution of bromine or a solution of permanganate when added to its solution in glacial acetic acid. It was crystallised from ether, when it had $[\alpha]_D^{18}$ + 27·4° in chloroform solution, and in melting point and chemical properties agreed exactly with the description given by Willstätter.

0·9740 gram was submitted to the ozone stream for sixty hours. The solution remained clear, and after evaporation of the bulk of the solvent in a vacuum the residue was kept in a vacuum at 38°. After three days the ozonide appeared as a very pale brown glass, the increase in weight amounting to 22 per cent. This gradually diminished until in three weeks the percentage increase was 17·5, and after five weeks the weight became constant:

0·9740 added 0·1256 O_2. Oxygen = 12·9.

$C_{27}H_{48}O\cdot O_3$ requires added oxygen = 12·4 per cent.

This substance, therefore, would appear to contain only one double linking in the molecule, a result in accordance with the theory that cholesterol contains two such linkings, and that in β-cholestanol one of these has been saturated by hydrogen, leaving one which reacts only with ozone.

β-Cholestanone.

This substance was first prepared and analysed by Diels and Abderhalden (*Ber.*, 1906, **39**, 884), and found to possess the formula $C_{27}H_{46}O$, so that it would appear to be the simple ketone corresponding with the alcohol β-cholestanol. It was readily obtained for these experiments by oxidation of the alcohol with chromic acid at 50°, and after crystallisation from acetone gave the correct melting point, 129°. As stated by Willstätter, the ketone rapidly decolorised a solution of bromine.

0·5106 gram of the ketone was ozonised for seventy hours. The solution remained quite clear throughout. After removal of the bulk of the solvent, the ozonide was kept in a vacuum at 38°. After two days the percentage increase of weight amounted to 27·2, and the ozonide appeared as an opaque, white, friable foam, and not as a glass. This gradually lost weight, until at the end of three weeks a constant value was obtained. The ozonide was now slightly yellow, and had a faint odour of orange oil:

0·5106 added 0·1280 O_2. Oxygen = 25·0.

$C_{27}H_{46}O \cdot O_6$ requires added oxygen = 24·8; $C_{27}H_{46}O \cdot O_7$ requires 29·1 per cent.

This ozone value points to the presence of two unsaturated linkings in the molecule of β-cholestanone, whereas, from the behaviour of the parent substance, only one would have been expected. The carbonyl group also does not appear to have taken up an atom of oxygen—the normal process according to Harries's observations. But he has also shown that in some cases, for example, when the carbonyl group is situated between two carbon atoms each of which is connected by a double linking to other groups, the addition of oxygen to it does not take place. Thus the substance $CMe_2{:}CH \cdot CO \cdot CH{:}CMe_2$ forms an ozonide by the addition of six, and not seven, atoms of oxygen.

Coprosterol, $C_{27}H_{48}O$.

This substance was formerly thought to be dihydrocholesterol, produced by the bacterial reduction of cholesterol in the human intestine. It is more probable, however, that the reactive side-chain of the cholesterol molecule becomes modified in some way with elimination of the double linking, so that coprosterol behaves as a saturated alcohol. The specimen used was a very pure one of human origin, prepared by hydrolysis of the acetate. It had a melting point of 99—100° and $[\alpha]_D^{20}$ +24°.

0·7938 gram was ozonised for fifty hours, the solvent being almost removed by the ozone stream. The solution remained clear throughout. After heating for one hour at 60°, the ozonide appeared as a clear, transparent glass full of gas bubbles, the increase of weight amounting to 15 per cent. After two further hours at 65°, the weight became constant:

0·7938 added 0·0974 O_2. Oxygen = 12·27.

$C_{27}H_{48}O \cdot O_3$ requires added oxygen = 12·36 per cent.

This ozonide was a clear glassy substance, which was quite unaffected after heating for several hours at 70°. On raising the temperature to 85°, however, decomposition set in, the glassy mass became full of gas bubbles, and a decided loss of weight took place. Prior to a constant weight being obtained, the fragrant odour previously mentioned was always observed on opening the flask, mingled in this case with a sharper odour, recalling that of *iso*butyric acid. The ozonide, after heating with water for four hours in a stream of air, evolved no carbon dioxide, but the fragrant odour was again noticed.

The results obtained point to the presence of one double linking in the molecule of coprosterol, which probably corresponds with the second double linking in the cholesterol molecule.

ψ-Coprosterol.

This substance is obtained by the action of sodium amyloxide on coprosterol, with which it is isomeric. On oxidation with chromic acid, it gives coprostanone (Trans., 1908, **91**, 1625). The specimen used, after recrystallisation from acetone, melted at 118—119°.

0·4588 gram was ozonised for fifty hours, at the end of which time traces of a gelatinous substance began to appear. The solution was pale yellow, and on evaporation left the ozonide as a pale brown glass. After heating in a vacuum for two hours at 70°, the increase in weight amounted to 29 per cent. After twelve hours' heating at this temperature, the weight became constant:

0·4588 added 0·1156 O_2. Oxygen = 25·2.

$C_{27}H_{48}O\cdot O_6$ requires added oxygen = 24·75 per cent.

At the beginning of the heating, the same fragrant odour was again observed, ceasing as the weight became constant. On keeping the ozonide at 80° for three hours, a loss of only 0·002 gram, or 0·4 per cent., in weight was observed. The ozonide, when boiled with water, evolved no carbon dioxide; the fragrant odour became very pronounced.

Coprostanone, $C_{27}H_{46}O$.

This ketone is obtained by the oxidation of coprosterol and ψ-coprosterol. On treatment with a chloroform solution of bromine, the bromine is instantly absorbed. The specimen used melted at 62—63°.

0·6167 gram was ozonised for twenty-four hours, at the end of which time it appeared fully saturated. The solution remained clear. After removal of the solvent and heating in a vacuum for twelve hours at 50°, the increase of weight amounted to 35 per cent. At the end of a further ten hours at 65°, the weight became constant:

0·6167 added 0·1802 O_2. Oxygen = 29·22.

$C_{27}H_{46}O{\cdot}O_7$ requires added oxygen = 29·01 per cent.

The ozonide was left as a transparent, homogeneous, pale brown glass. It lost no weight on further heating at 75° for two hours. The percentage of oxygen added corresponds exactly with that required for a ketone containing two unsaturated linkings.

α-Cholestanol, $C_{27}H_{46}O$ (?).

This alcohol was originally obtained by Diels and Abderhalden (*loc. cit.*) by the action of sodium in amyl-alcoholic solution on cholesterol. It behaved as a saturated compound, and was regarded as a reduction product of cholesterol. Later, Windaus (*Ber.*, 1907, **40**, 2637), in the course of some experiments carried out with the object of condensing the unsaturated side-chain of cholesterol to a new ring, found that on heating cholesterol with ready-formed sodium amyloxide, α-cholestanol was also produced. He considered it most probable, therefore, that α-cholestanol is not a reduced product, but an isomeric saturated *cyclo*cholesterol (Formula IV).

If the isomerising action of the sodium amyloxide is limited to a modification of the side-chain in this way, α-cholestanol should still retain the obscure double linking of the cholesterol molecule and form an ozonide.

The specimen employed was prepared by Windaus's method. It exhibited the characteristic melting-point phenomena described by Diels and Abderhalden.

0·4473 gram was ozonised for twenty-four hours. After removal of the solvent, the residue had a crystalline appearance quite different from that of the other ozonides. After heating in a vacuum at 50° for half-an-hour, the weight became constant and equal to the original weight of substance taken. The residue was dissolved in acetone, from which it crystallised well, and the substance on heating in a capillary tube sintered at 118°, shrank at 124°, and melted to a clear liquid at 128—129°, agreeing exactly in these respects with the original substance. α-Cholestanol therefore does not react with ozone, and would accordingly seem to contain no unsaturated linkings, so that the change brought about by the isomerising agent must have included that part of the molecule which contains the second double linking. If this is so, it was thought possible that the dibasic acid, $C_{27}H_{44}O_4$ (Formula II), might also be affected by sodium amyloxide, but on heating five grams of the acid for eight hours with this reagent the whole of the acid was recovered unaltered.

The Action of Bromine on β-Cholestanone and Coprostanone.

The reaction with ozone just described points to the presence of two unsaturated linkings in these ketones, which are prepared from the corresponding alcohols by oxidation with chromic acid at 50°. The alcohols are indifferent to bromine, whereas the ketones rapidly absorb it. In the case of β-cholestanone, an attempt was first made to determine approximately its bromine absorption by titration with an $N/2$-solution of bromine in chloroform. The addition of the first few c.c. of the bromine solution to a chloroform solution of the ketone produced a deep brown colour, which persisted for perhaps a minute and then suddenly disappeared. Subsequently the bromine was decolorised instantly, and the titration was continued until the brown tint persisted for twenty minutes. In this way, the bromine absorbed per molecule of ketone was found in two experiments to be 314 and 341 respectively; an absorption of $2Br_2$ would require 320. During the course of the addition of the bromine solution, however, quantities of hydrogen bromide were evolved, so that, at any rate in part, a substitution of bromine must have taken place. The titrated solutions, which contained 0·5 gram of the ketone and still contained a slight excess of bromine, were at once evaporated to dryness at a gentle heat. The product obtained consisted of at least two substances. It dissolved sparingly in boiling light petroleum, and the solution on cooling deposited long, white needles (A). These were sparingly soluble in light petroleum and almost insoluble in alcohol. After re-crystallisation the compound melted and decomposed at 188°. The filtrate from A dried to a mass of long needles, which were very soluble in light petroleum, but more sparingly so in alcohol, from which the substance crystallised in small, white spherules. These melted at 139—140°, and showed no signs of decomposition (B). The alcoholic mother liquors from this deposited a considerable quantity of an amorphous, yellowish-brown substance. The compounds A and B both gave a well-marked qualitative test for bromine, and to obtain them in quantity sufficient for analysis 5 grams of the ketone were treated in chloroform solution with twice the quantity of bromine required according to the above experiments, and the mixture kept for twenty-four hours. The action, however, in this case proceeded on different lines. The product obtained was a sticky, amorphous solid, very soluble in light petroleum or acetone, but insoluble in alcohol. After solution in acetone and precipitation by alcohol, it was obtained colourless. It gave the test for bromine, but melted indefinitely between 85° and 95° without apparent decomposition. It no doubt consisted of a mixture of amorphous bromine compounds similar to those obtained by the action of bromine on cholesterol, and was not analysed. In the absence of further material, it was not possible to continue these experiments. It was found, however, that the ketone did not absorb iodine when treated with Hübl's iodine solution. Under the same conditions, cholesterol gave a correct iodine value. The double bonds revealed by the ozone test in this ketone are not therefore very reactive, and bromine would seem to act as a substituent.

Coprostanone.

This ketone, when treated with a chloroform solution of bromine, at once decolorised it, and the addition of the bromine was continued until a permanent brown tint remained. Quantities of hydrogen bromide were evolved, so that in this case also substitution occurs. The excess of bromine was, after a short time, removed by means of aqueous sulphurous acid, and after the separation of this the chloroform was removed at a low temperature. The product was purified by solution in acetone and precipitation with alcohol, by which means it was obtained colourless. It was then dissolved in acetone, mixed with a little alcohol, and the solution allowed to evaporate at the ordinary temperature. In two days a crop of large, isolated prisms was obtained, which were very hard and gritty. After several re-crystallisations, the substance melted at 127—128° to a clear liquid, which only began to decompose at 150°:

0·1447 gave 0·1013 AgBr. Br = 29·8.

$C_{27}H_{44}OBr_2$ requires Br = 29·4 per cent.

This result, taken in conjunction with the observed evolution of hydrogen bromide during the preparation and the fact that the ketone did not absorb iodine from Hübl's iodine solution, indicates that the action of bromine on coprostanone is to produce a dibromo-substitution derivative. The double bonds which react with ozone are indifferent therefore towards the action of bromine.

The Ozonide of Phytosterol.

In a recent paper (Trans., 1908, **93**, 1928), Pickard and Yates have shown that phytosterol in all probability contains an unsaturated side-chain similar to that present in cholesterol. With the view of demonstrating this fact by a method similar to that previously employed in the case of cholesterol (Trans., 1908, **93**, 1328), the ozonide of phytosterol was prepared. The phytosterol was obtained from wheat germ according to the instructions of Burian (*Monatsh.*, 1897, **18**, 551), and after crystallisation from ethyl acetate melted at 137·5°. After saturation with ozone in chloroform solution, the bulk of the solvent was evaporated, and the white residue at once heated with water in a current of air as already described. Carbon dioxide was evolved regularly and in considerable quantity, a decomposition which indicates that an unsaturated linking is present which is situated at the end of a side-chain of carbon atoms.

Summary and Conclusions.

1. The action of ozone on the cholesterol derivatives studied in the course of this investigation is exhibited in the following table:

	Ozonide.
Cholesterol, $C_{27}H_{46}O$	$C_{27}H_{46}O{\cdot}O_6$
Cholestenone, $C_{27}H_{44}O$	$C_{27}H_{46}O{\cdot}O_7$
	$C_{27}H_{46}O{\cdot}O_4$
Dibasic acid, $C_{27}H_{44}O_4$	$C_{27}H_{44}O_4{\cdot}O_8$
	$C_{27}H_{44}O_4{\cdot}O_3$
β-Cholestanol, $C_{27}H_{48}O$	$C_{27}H_{48}O{\cdot}O_3$
β-Cholestanone, $C_{27}H_{46}O$	$C_{27}H_{46}O{\cdot}O_6$
Coprosterol, $C_{27}H_{48}O$	$C_{27}H_{48}O{\cdot}O_3$
ψ-Coprosterol, $C_{27}H_{48}O$	$C_{27}H_{48}O{\cdot}O_6$
Coprostanone, $C_{27}H_{46}O$	$C_{27}H_{46}O{\cdot}O_7$
α-Cholestanol, $C_{27}H_{46}O$	None

All these compounds dissolve readily in ethyl acetate, and are precipitated on the addition of light petroleum.

2. The determination of the ozone value of these compounds has certainly led to results which do not disagree with the view that cholesterol may contain two unsaturated linkings, but in no case was the method of heating to 60° in a vacuum found to be so simple and expeditious as in the case of cholesterol and phytosterol. The reason for this is that the ozonides obtained are, for the most part, comparatively high melting substances, which, at the beginning of the heating, retain sufficient of the solvent to cause them to flow over the walls of the containing vessel, and they then solidify in the form of a hard, smooth glass. It is obvious that this glass, unless heated to its softening point, will still retain quantities of the heavy chloroform sufficient to invalidate any quantitative measurement; and if so heated the ozonide is itself liable to decompose with loss of oxygen. The ozonides examined, however, are on the whole very stable, and generally do not seem to be affected at temperatures below 80—85°. The fact that many of them became pale brown would seem to be due rather to

the action of the ozone than to that of heat. It was observed that where the action of the ozone had been very prolonged a yellow or brown product was always produced. Those ozonides, on the other hand, which were formed by the limited action of the ozone stream, as, for example, the acid ozonide, $C_{27}H_{44}O_4{\cdot}O_3$, were pure white, and continued so during the heating to constant weight.

3. If the action of ozone be regarded as a method for the recognition of unsaturated linkings in organic compounds which can be relied on when all others have led to negative results, and if the experimental facts as described above be accepted as correct, we are certainly justified in agreeing with the conclusion of Molinari that cholesterol contains in its molecule a second and previously unsuspected double linking. Thus cholesterol adds two molecules of ozone and therefore contains two such bonds; β-cholestanol, its dihydro-derivative, combines with one molecule of ozone, and therefore still contains one double bond; in the case of coprosterol, in which the unsaturated side-chain is probably not simply reduced, but also modified, one double linking is also shown to be present. The behaviour of the acid $C_{27}H_{44}O_4$, and less clearly that of cholestenone, moreover, throws some light on the mechanism of the action of ozone. In the case of the acid, which still contains the reactive unsaturated side-chain of the cholesterol molecule, but which has hitherto been found to behave chemically as a saturated compound, the first effect of ozone is to produce a mono-ozonide in which the molecule of ozone has attached itself at the position of the double linking situated in the side-chain. Then slowly and sluggishly ozone is absorbed until a compound, $C_{27}H_{44}O_4{\cdot}O_8$, is obtained, this number of oxygen atoms being that required theoretically (according to Harries) for a doubly unsaturated dibasic acid. The behaviour of the ketones, β-cholestanone and coprostanone, although definite, is somewhat unexpected. The ozone value appears to indicate that they each contain two unsaturated linkings, whereas the mother substances contain but one. The oxidation is effected smoothly at a low temperature, but apparently a second double linking is developed. This conclusion is supported by the observed fact that the ketones absorbed bromine, but an examination has shown that the action of bromine is one of substitution, and in the case of coprostanone a dibromo-substitution derivative was obtained in a crystalline form.

3. The action of sodium amyloxide on both cholesterol and cholestenone results in the formation of the so-called α-cholestanol (compare Trans., 1908, **93**, 1628). This derivative alone among

those examined did not react with ozone, and therefore, unlike the others, cannot be considered to contain an unsaturated linking. That the reagent used in its preparation has a reducing action is shown by Diels's observation that cholestenone is likewise converted into α-cholestanol under the influence of sodium amyloxide. It may be therefore that the action of sodium amyloxide on cholesterol is not simply to produce a linking up of the unsaturated side-chain, but that the second double linking is simultaneously reduced. Here again, however, a contradiction is noticed, since β-cholestanol, which is, one must suppose from its original method of formation (*Ber.*, 1906, **39**, 884), stable towards sodium amyloxide, still forms a mono-ozonide.

4. In this connexion it is of interest to recall the observations of Hausmann (*Beitr. chem. Physiol. Path.*, 1905, **6**, 567) and Abderhalden and Le Count (*Zeitsch. exp. Path. Ther.*, 1905, **2**, 199), who have shown that the antitoxic action exhibited by the naturally occurring cholesterols towards hæmolytic poisons such as saponin ceases if the hydroxyl group is esterified, and is reduced to a minimum if the double linking be saturated, as in cholesterol dichloride, or modified as in coprosterol and some other synthetic products similar to α-cholestanol. Windaus (*Ber.*, 1909, **42**, 238) has recently shown that this antitoxic effect is probably due to the ready formation of a compound between the saponin and cholesterol. Working with digitonin, he found that it formed crystalline compounds with cholesterol and phytosterol with the greatest ease; further, that the saturated β-cholestanol and coprosterol also combined, but that α-cholestanol, which still contains the hydroxyl group, formed no such compound. If it be assumed, as previously considered, that a double linking and a hydroxyl group are necessary for the performance of the anti-hæmolytic function, we have here an explanation of the fact that coprosterol has a feeble anti-hæmolytic action towards saponin (due to the weak reactivity of the second double linking), and that α-cholestanol, which does not contain a double linking at all, has no power of combination with saponin, and could not therefore act as an antitoxin.

5. Although there is thus good reason for the hypothesis that a second double linking is present in the cholesterol molecule, it must be said that in no case has there previously been any reason to infer the presence of such a linking from chemical considerations. The exhaustive researches of Windaus (compare *Arch. Pharm.*, 1908, **246**, 117) have resulted in the following breaking down of the cholesterol molecule. The acid $C_{27}H_{44}O_4$ (I) has been converted into the tricarboxylic acid, $C_{25}H_{40}O_6$ (II):

$$\underset{\text{(I.)}}{CO_2H\cdot CH_2\cdot C_{22}H_{37}(CO_2H)\cdot CH\dot{:}CH_2},\qquad \underset{\text{(II.)}}{C_{22}H_{37}(CO_2H)_3},$$

$$\underset{\text{(III.)}}{C_{17}H_{26}(CO_2H)_4},$$

and from the complex $C_{22}H_{37}$ an *iso*amyl group has been removed by oxidation, resulting in the formation of a tetrabasic acid, $C_{21}H_{30}O_8$ (III) (*Ber.*, 1908, **41**, 2566). All these changes have been exactly followed step by step, and require for their explanation only the presence of the original well-known double linking. The acid $C_{21}H_{30}O_8$ again is extraordinarily stable under the most violent chemical treatment, and Windaus regards it as extremely improbable that it should contain double bonds. Especially considering the sluggish manner in which the complete ozonisation of the cholesterol derivatives has been found to take place compared with the readiness with which the original double linking reacts, it may be, therefore, that the further action of ozone consists in the development of a bridge or cross linking, or the opening up of a polymethylene ring present in the cholesterol molecule.

PART II.—*The Reaction between Coprostanone and Phenylhydrazine.*

In a former paper (Trans., 1908, **93**, 1629), in which the preparation and properties of coprostanone were described, this ketone was found to react readily with phenylhydrazine in glacial acetic acid solution, but the resulting compound gave numbers on analysis which differed widely from those of the anticipated phenylhydrazone, and pointed rather to a condensation having taken place with separation of ammonia. The compound has now been obtained in considerable quantity, and its properties have been further investigated. It is a pure white, crystalline substance readily soluble in ether, acetone, or chloroform, moderately so in benzene, and sparingly so in glacial acetic acid, light petroleum or alcohol. It melts at 191° without decomposition, and readily absorbs bromine in chloroform solution.

It was shown originally by Drechsel (*J. pr. Chem.*, 1888, [ii], **38**, 69) that *cyclo*hexanonephenylhydrazone, when warmed with dilute mineral acids, was not resolved into *cyclo*hexanone and phenylhydrazine, but instead evolved a molecule of ammonia with the formation of tetrahydrocarbazole. This reaction is obviously a special case of the indole synthesis from aldehyde- and ketone-phenylhydrazones described by Emil Fischer, but, unlike these, it is induced easily and without the use of energetic methods.

This is ascribed by Borsche (*Annalen*, 1908, **359**, 49) to the fact that the carbonyl group is present in a reduced ring, and in the course of a lengthy investigation (*loc. cit.*) he has shown generally that the phenylhydrazones of hydroaromatic ketones readily undergo this condensation when treated with dilute acids, with the formation of tetra- and hexa-hydrocarbazole compounds. The tetrahydro-derivatives can easily be reduced to hexahydro-compounds, and, on heating gently with lead oxide, hydrogen can be removed with the formation of carbazoles.

A consideration of these facts makes it very probable that a similar change takes place even more easily in the case of coprostanone, and that the glacial acetic acid used as a solvent acts on the coprostanonephenylhydrazone at the moment of its formation with elimination of ammonia and the production of a *coprosterylcarbazole*, thus:

$$C_{27}H_{46}O + C_6H_5\cdot NH\cdot NH_2 = C_{33}H_{49}N + NH_3 + H_2O.$$

That this is the correct explanation will appear from the following:

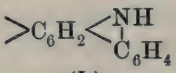
(i) The formula $C_{33}H_{49}N$ corresponds very well with the analytical results previously published. The mean of five carbon and hydrogen determinations and three nitrogen estimations gave:

$C=86{\cdot}5$; $H=10{\cdot}9$; $N=3{\cdot}5$.

$C_{33}H_{49}N$ requires $C=86{\cdot}3$; $H=10{\cdot}7$; $N=3{\cdot}05$ per cent.

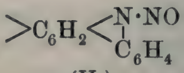
(ii) The presence of ammonia in the acetic acid mother liquors of the various preparations was readily demonstrated. On treatment with alkali, the gas was evolved in quantity and was easily recognised.

(iii) Coprosterylcarbazole may accordingly be represented by the following schematic formula (I):



$>C_6H_2<\begin{matrix}NH\\ | \\ C_6H_4\end{matrix}$

(I.)



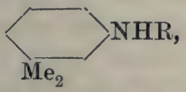
$>C_6H_2<\begin{matrix}N\cdot NO\\ | \\ C_6H_4\end{matrix}$

(II.)

(iv) The imino-group was characterised by the formation of a nitroso-derivative (II). For this preparation 3 grams of the compound were dissolved in 25 c.c. of ether, and mixed with 25 c.c. of acetic acid of sp. gr. 1·04. Six grams of solid potassium nitrite were then added to the cooled mixture. The originally colourless solution at once became deep yellow, and an orange-yellow, crystalline solid separated, which was collected and washed with ether, in which it was quite insoluble. The yield was nearly quantitative. The *nitroso*-compound was of a bright orange colour, very soluble in benzene, but almost insoluble in acetone, alcohol or light petroleum. When crystallised several times from a mixture of benzene and light petroleum it was obtained in short, stout rods or plates. On heating, it shrank and turned red at 148°, and melted and decomposed at 158° to a dark red liquid:

0·1479 gave 0·4401 CO_2 and 0·1271 H_2O. C=81·15; H=9·55.
0·1681 ,, 8·4 c.c. N_2 (moist) at 757 mm. and 13°. N=5·88.
$C_{33}H_{48}ON_2$ requires C=81·15; H=9·84; N=5·74 per cent.

For the determination of carbon and hydrogen, lead chromate and a silver spiral were used. For the nitrogen estimation, the substance was mixed with cuprous chloride, as the previous estimations with the original substance gave high values for nitrogen. It was thought not impossible that this might be due to causes similar to those investigated by Haas (Trans., 1906, **89**, 570), who found that bases containing the grouping:



in which two methyl groups were attached to the same carbon atom, gave a certain amount of methane on combustion in the ordinary way. The presence of a similar arrangement in coprosterol is by no means improbable, as bacterial action in the intestine might conceivably convert the unsaturated side-chain of cholesterol into two methyl groupings, thus:

$$>CH\cdot CH:CH_2 + H_2 \longrightarrow >C(CH_3)_2.$$

In conclusion, I wish to express my thanks to Professor Adolf Windaus, of Freiburg, for his great kindness and courtesy in sending me a quantity of the acid $C_{27}H_{44}O_4$, and explaining to me the improvements he has made in its method of preparation.

The expenses of this investigation have been covered by a grant made by the Government Grant Committee of the Royal Society, for which I take this opportunity of expressing my thanks.

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LXXIX—*Iodine Dioxide.*

By Matthew Moncrieff Pattison Muir.

Millon, in 1844 (*Ann. Chim. Phys.*, [iii], **12**, 333), described the preparation of an oxide of iodine, to which he gave the formula I_2O_4, by the interaction of nitric acid and iodine, and also by the interaction of hot concentrated sulphuric acid and iodic acid. I shall embody the results of my examination of Millon's second method for preparing the oxide in directions for the preparation of the compound.

Preparation of Iodine Dioxide.—To about 60 grams of powdered iodic acid, in a platinum dish, about 200 grams of concentrated sulphuric acid are added, and the mixture is heated and stirred. When oxygen has been evolved freely for a few minutes, and the liquid is dark brownish-yellow, the flame is lowered, and as soon as the vapours show a slight violet tint, the heating is stopped. This part of the process occupies ten or fifteen minutes. After cooling, the dish is kept for five or six days over sulphuric acid. The liquid is then poured off from the yellow, crystalline crust which has formed, the solid is powdered, and the powder is washed by the help of a little of the liquid before poured off into a funnel stopped with glass-wool, and drained by the aid of the pump. The solid is now transferred to a dry, porous tile, and kept in a desiccator for about a week, the solid being occasionally removed, rubbed to a fine powder, and replaced on the tile. When it is found, by making a trial with a little of the solid, that shaking for a minute or so with a very little cold water does not cause the separation of more than a minute quantity of iodine, the yellow solid is transferred to a funnel stopped with glass-wool, washed quickly with successive small quantities of cold water by the aid of the pump until the washings are free from sulphate (five or six washings generally suffice), and then with small quantities of absolute alcohol until the washings are quite colourless. The solid is then washed twice or thrice with dry ether, the washing liquid is removed as completely as possible by suction, the solid is placed on a porous tile which is kept over dry lime for a few days, and is then dried at 100°.

Taking the reaction of preparation to be $2HIO_3 - H_2O - O = I_2O_4$, about 30 per cent. of the theoretical yield of the dioxide can be obtained by working with moderate care.

Analysis of Iodine Dioxide.—For the analysis of this compound, I used a modification of the process described by Chrétien, in

1898 (*Ann. Chim. Phys.*, [vii], **15**, 364), based on the fact that iodic anhydride reacts with an aqueous solution of oxalic acid in the presence of sulphuric acid at 100° to give carbon dioxide, water, and iodine.

A flask of about 250 c.c. capacity was employed, into the neck of which was ground a glass stopper, carrying an entrance tube leading nearly to the bottom of the flask, and an exit tube; the exit tube was connected with two glass-stoppered bottles containing an aqueous solution of potassium iodide, and surrounded by cold water. A weighed quantity of the compound was placed in the flask, dilute sulphuric acid and a measured volume of normal oxalic acid solution were added, a stream of washed carbon dioxide was kept passing through the apparatus, and the contents of the flask were boiled until iodine had ceased to pass over with the steam and the liquid in the flask was colourless. The iodine was estimated by standard thiosulphate, and the residual oxalic acid by standard permanganate solution.

The following are the percentages of iodine and oxygen found by this method. The specimens of iodine dioxide were prepared at different times; two of them were dried at 100°, the other two at 115°:

Found:	I = 80·97	81·29	80·39	80·96	Mean	= 80·90
	O = 20·17	19·93	20·09	20·80	,,	= 20·25

I_2O_4 requires I = 79·87; O = 20·13 per cent.

As the calculation assumes that the whole of the iodine of the compound is set free in the reaction, and that the oxygen which oxidises oxalic acid comes only from the compound, the results of the analyses demonstrate the accuracy of the equation:

$$I_2O_4 + 4H_2C_2O_4 = I_2 + 4H_2O + 8CO_2.$$

Iodine dioxide reacts slowly with cold water, and quickly with hot water, to produce iodine and iodic acid. This reaction suggested another method for analysing the compound. A weighed quantity was boiled with water in a stream of washed hydrogen, the iodine was led into potassium iodide solution, and the iodic acid was estimated in the colourless liquid left in the flask by titration with standard sodium hydroxide solution, phenolphthalein being used as indicator. Assuming the reaction to be represented by the equation:

$$5I_2O_4 + 4H_2O = 8HIO_3 + I_2,$$

the percentage of iodine dioxide can be calculated (1) from the quantity of iodine set free, and (2) from the quantity of iodic acid produced. The following results were obtained:

(1) From iodine: 98·88, 100·50 per cent. I_2O_4. (2) From iodic acid: 99·83, 100·19, 100·50 per cent. I_2O_4.

The results of the two sets of analyses show, I think, that the composition of the oxide is IO_2 (or I_2O_4). The results of the second series of analyses demonstrate the accuracy of the equation:

$$5I_2O_4+4H_2O=8HIO_3+I_2.$$

Properties and Reactions of Iodine Dioxide.—Iodine dioxide is a lemon-yellow solid; when allowed to separate slowly from its solution in hot concentrated sulphuric acid, it appears under the microscope as a mass of minute, pale yellow, crystalline rosettes. The compound is not hygroscopic. Specific gravity 4·2 at 10° referred to water at the same temperature. As the molecular weight of the compound has not been determined, the formula may be written either IO_2 or I_2O_4. Decomposition begins at about 130°; the products are iodine and oxygen.

Iodine dioxide is insoluble in, and is unacted on by, dry ether or glacial acetic acid; it dissolves very slowly and very slightly in monochloroacetic acid or acetone. When kept in contact with phenol, aniline, or pyridine, iodine is very gradually formed and dissolved, and a little iodine pentoxide is produced. Absolute alcohol reacts slowly with iodine dioxide; iodine passes into solution, and iodine pentoxide remains. The reaction is so slow that a gram of the compound is not wholly changed until it has been kept in contact with alcohol for about four months. The compound is changed to iodine and iodic acid by the action of cold nitric acid, whether concentrated or dilute. When shaken with cold concentrated hydrochloric acid, chlorine is given off, and a yellow solution is formed; when the liquid is heated, much chlorine is produced; there is no separation of iodine; the solution contains iodic acid and, probably, iodine chloride, but, after boiling with considerable excess of hydrochloric acid for some time, the iodic acid is entirely decomposed.

The action of cold dilute sulphuric acid is slow; the final products are iodine and iodic acid. Boiling dilute sulphuric acid reacts in the same way as boiling water; the equation given on p. 657 was verified quantitatively, excess of dilute sulphuric acid being used. When iodine dioxide is slightly moistened with concentrated sulphuric acid and left exposed to the air, iodine and iodic acid are gradually formed. Cold concentrated sulphuric acid (about 99 per cent. H_2SO_4) dissolves the compound slowly. I found that 100 c.c. of this acid dissolve 1·54 grams of iodine dioxide at 15—20°. Sulphuric acid of the concentration H_2SO_4,H_2O dissolves iodine dioxide more freely than 99 per cent. acid; a little iodine is produced and dissolved, and the solution contains some iodic acid. When the oxide is heated with concentrated sulphuric acid, a little iodine is given off.

Fuming sulphuric acid dissolves iodine dioxide. When heated, the liquid becomes green, and then gradually yellow; no iodine is given off. On cooling, a yellow solid is deposited, which, after washing with alcohol and drying at 100°, was found to contain 93 per cent. iodine dioxide mixed with a little iodine pentoxide. Therefore, fuming sulphuric acid dissolves iodine dioxide and oxidises some of it to pentoxide. No distinct evidence was obtained of the formation of compounds of iodine dioxide and sulphuric acid.

Aqueous potassium hydroxide reacts with iodine dioxide to form potassium iodate and iodide in accordance with the equation:

$$3I_2O_4 + 6KOH = 5KIO_3 + KI + 3H_2O.$$

The accuracy of this presentation of the reaction was proved by shaking a weighed quantity of the oxide with a measured volume, being a considerable excess, of standard potassium hydroxide solution, and determining the amount of alkali unacted on by titration with standard acid; also by adding a slight excess of nitric acid to a solution of the oxide in potassium hydroxide, precipitating by silver nitrate solution, adding more nitric acid, boiling, and weighing the silver iodide. The results of applying these methods were very fairly satisfactory. For instance, 1·1275 grams of iodine dioxide were dissolved in 150 c.c. of $N/5$-potassium hydroxide solution; 112 c.c. of the potash solution remained unacted on; therefore, 38 c.c. of $N/5$-potash were used to react with the oxide, and this is equivalent to 1·2084 grams of I_2O_4 if the equation given above is correct. In another experiment, 0·1877 gram of the oxide was used, and 0·1846 gram was found. In another experiment, 0·0650 gram potassium iodide was found in the solution of 0·3754 gram iodine dioxide in potash, and the equation required that 0·0653 gram potassium iodide should have been produced.

Interaction of Iodine Dioxide and Sulphur Trioxide.—A quantity of iodine dioxide, weighing 1·02 grams, was placed in a weighed Λ-shaped tube; sulphur trioxide, prepared by heating fuming sulphuric acid, was passed into the tube, which was sealed off and weighed; the weight of sulphur trioxide added was 1·25 grams. The ratio of the two oxides was nearly $I_2O_4 : 5SO_3$. The tube was heated to 80° for eight hours; excess of sulphur trioxide was then distilled off into the other limb of the tube; the tube was cut; that part of it which contained the solid matter was kept in a desiccator over lime for some days, and then weighed. The contents of the tube were washed out, and the tube was weighed. The weight of the solid matter in the tube was 1·789 grams; hence the weight of sulphur trioxide which had combined with 1·02 grams of iodine dioxide was 1·789 – 1·02 = 0·769 gram. The ratio 1·02 : 0·769 is the same as 318 : 239·7; that is to say, the results of this experiment point to the formation of the compound $I_2O_4,3SO_3$ (ratio = 318 : 240).

The following method was adopted as the result of many attempts to discover the most suitable conditions for the preparation of a compound of iodine dioxide and sulphur trioxide. About 20 grams of sulphur trioxide are distilled into a tube of good glass, about 300 mm. long, sealed at one end and narrowed near the other end; from 5 to 8 grams of iodine dioxide are shaken into the tube, which is then sealed. The tube is almost wholly immersed in water, in an upright position, and heated to 85—90° for about twenty-four hours until an apparently homogeneous, pale yellow solid is obtained, covered by a yellowish-green liquid. While still hot, the tube is reversed and allowed to drain for some time; the tube is now cut, and the portion which contains the yellow solid is at once placed in a wide tube and heated to 90° in a slow stream of dried carbon dioxide until fumes of sulphur trioxide have almost ceased to appear, usually for about six hours. The solid in the tube is quickly powdered, and heated in dried carbon dioxide at 95—100° until sulphur trioxide has entirely ceased to be evolved. The solid is then quickly transferred to a weighing tube and kept in a desiccator.

Analysis of the Compound of Iodine Dioxide and Sulphur Trioxide.—By dissolving the compound in dilute potassium hydroxide solution, reducing iodate to iodide by sulphur dioxide, removing excess of the latter by boiling, and precipitating silver iodide, after acidifying by nitric acid, the percentage of iodine found was 47·15. The formation of a compound, $I_2O_4,3SO_3$, was indicated by the experiment described in the last section; this formula requires I = 45·52 per cent. The most concordant results were obtained by using Chrétien's method (described on p. 657), namely, boiling with sulphuric acid and a measured volume of standard oxalic acid, leading the iodine into a solution of potassium iodide, and determining the amount of oxalic acid oxidised by the oxygen combined with iodine in the compound.

The sulphur trioxide of the compound was determined by dissolving in hydrochloric acid, adding iron wire, warming for some time, and then precipitating by a solution of barium chloride (compare Kämmerer, *J. pr. Chem.*, 1861, **83**, 73). Complete analyses were made of two specimens of the compound, and partial analyses of four other specimens. The following percentage quantities of the components were found:

I =	44·25	47·22	41·55	41·05	Mean = 43·51
O =	10·04	10·94	9·96	11·50	,, = 10·61
SO_3 =	45·20	41·27	40·98	43·12	,, = 42·64

$I_2O_4,3SO_3$ requires I = 45·52 ; O = 11·47 ; SO_3 = 43·01 per cent.
$2I_2O_4,7SO_3$,, I = 42·47 ; O = 10·70 ; SO_3 = 46·83 ,,

The product of the reaction between the two oxides is very hygroscopic, and it is possible that more than one compound is formed in the reaction; these considerations account, in my opinion, for the discrepancies in the analytical data. The analyses prove, I think, that the formula $I_2O_4,3SO_3$ expresses the composition of the main, if not the only, product of the interaction which occurs when iodine dioxide and sulphur trioxide are heated together to 85—90°, and the solid which is formed is heated to 95—100° in a stream of dried carbon dioxide until sulphur trioxide ceases to be evolved. This conclusion is strengthened by the results of weighing the quantities of the two oxides and the quantity of the compound formed by their union (see p. 660), and also by the estimation of iodine in the compound by precipitation as silver iodide (see p. 660).

Properties and Reactions of the Compound $I_2O_4,3SO_3$.—The compound is a pale yellow solid; a specimen of it was unchanged after keeping in a corked tube in a desiccator for three months. When heated, iodine, oxygen, and sulphur trioxide begin to be evolved at about 120°; after heating to 190° for a few minutes, the residue contains a considerable quantity of sulphur trioxide. The compound is very hygroscopic; when exposed to the air for a short time, iodine separates, and after a day or two a white, crystalline solid is formed, which was proved to be iodic acid; a few yellow specks remained after exposure to the air of about half a gram of the compound for three months. When shaken with cold water, in very small quantities at a time, sulphur trioxide is removed, along with a little iodine, and iodine dioxide remains mixed with traces of iodic acid. The compound dissolves in a large quantity of cold water, the water becoming coloured by dissolved iodine; the solution contains iodic and sulphuric acids. When the compound is added slowly, in very small quantities at a time, to about twenty times its weight of absolute alcohol, cooled continuously by running water, almost the whole of it dissolves, forming a slightly yellow liquid, which becomes gradually more deeply coloured on standing; iodine and sulphur trioxide were found in the solution; after a few days a very small quantity of a yellow solid remained, which was proved to be iodine dioxide. Crystals of iodic acid were obtained by allowing the solution in alcohol to evaporate at the ordinary temperature. Ether very slowly dissolves sulphur troxide from the compound, and, finally, leaves iodine dioxide.

Compound of Iodine Pentoxide and Sulphur Trioxide.—As Kämmerer (*J. pr. Chem.*, 1861, **83**, 73) stated that a compound of iodine pentoxide and sulphur trioxide, to which he gave the formula $5I_2O_5,SO_3$, is formed by passing dried sulphur dioxide over iodine pentoxide at 100°, and as Weber (*Ber.*, 1887, **20**, 87) described a compound of the composition $I_2O_5,3SO_3$, I thought it advisable to determine whether iodine pentoxide and sulphur trioxide combine when heated to 100°. About 5 grams of iodine pentoxide (I_2O_5) were heated in a sealed tube with about four times its weight of sulphur trioxide in the manner described on p. 660 for about twenty-four hours. When most of the excess of sulphur trioxide had been poured off, the residual solid was heated to 90° in a slow stream of dried carbon dioxide until sulphur trioxide ceased to be given off; it was then quickly powdered, and again heated to 100° in carbon dioxide so long as any traces of sulphur trioxide were evolved. A pale yellow, hygroscopic solid, closely resembling the compound $I_2O_4,3SO_3$, was thus obtained. The substance was analysed by the method described on p. 660.

The following results were obtained:

Found:	I = 51·67	51·87	Mean =	51·77
	O = 17·18	15·69	,, =	16·43
	SO_3 = 32·16	33·89	,, =	33·02

$I_2O_5,2SO_3$ requires I = 51·42; O = 16·19; SO_3 = 32·39 per cent.

These results prove, I think, that a compound of iodine pentoxide and sulphur trioxide is formed by heating these compounds to about 100°, and make it very probable that the compound formed in my experiments had the composition $I_2O_5,2SO_3$. The formation and fair stability towards heat of the compounds $I_2O_4,3SO_3$ and $I_2O_5,2SO_3$ show that both of the oxides of iodine have slightly basic properties, and emphasise the connexion between iodine and manganese, elements which the periodic system of classification places in the same group.

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LXXX.—iso*Amygdalin and the Resolution of its Hepta-acetyl Derivative.*

By Frank Tutin.

It was shown by J. W. Walker (Trans., 1903, **83**, 472) that, under certain conditions, amygdalin yields inactive mandelic acid on hydrolysis, instead of the lævo-isomeride. If, for example, amygdalin be directly hydrolysed with concentrated hydrochloric acid, *l*-mandelic acid is formed, but if it be first hydrolysed to amygdalinic acid and the latter subsequently treated with hydrochloric acid, the resulting mandelic acid is optically inactive. Walker also demonstrated that the racemisation of the mandelic part of the molecule does not occur during hydrolysis, but that this takes place whenever amygdalin is dissolved in dilute solutions of an alkali. He concluded, therefore, that amygdalinic acid is partially racemic, but did not ascertain definitely the nature of the product formed by the action of dilute alkalis on amygdalin.

The subject in question was studied more fully by H. D. Dakin (Trans., 1904, **85**, 1512), who showed that amygdalin, when treated with dilute aqueous alkalis, is converted into an optically isomeric product, which was designated *iso*amygdalin. He confirmed the observation of Walker that amygdalinic acid, on hydrolysis, yields inactive mandelic acid, but found that the mandelic acid prepared by the acid hydrolysis of *iso*amygdalin always had a small dextro-rotation. These facts have also been confirmed by the present author.

Dakin, however, considered it highly improbable that the preponderance of *d*-mandelic acid yielded by *iso*amygdalin was due to the latter being "a mixture of *i*-mandelonitrile maltoside and *d*-mandelonitrile maltoside." He, therefore, offered the explanation that it was due to the occurrence of both racemisation and hydrolysis, the derivative of the *d*-mandelonitrile undergoing the latter change more rapidly than that of the *l*-nitrile. During the course of hydrolysis, therefore, the unchanged part of the material would contain a preponderance of the latter derivative, and this, he considers, would undergo some racemisation, the final result being the production of more *d*-mandelic acid than of its optical antipode.

It appears to the present author, that of these two explanations, the one preferred by Dakin is not the correct one. When an optically active compound is completely racemised, the resulting optical antipodes are, of course, formed in equal proportions, but when one asymmetric carbon atom suffers racemisation in a molecule containing other asymmetric groups, which are stable, the latter may influence the relative proportions of the constituents of the resulting mixture. Thus it was shown by Barrowcliff (Trans., 1907, **91**, 875) that the "dextro-menthone" of Beckmann, formed from *l*-menthone by the racemisation of one of its asymmetric carbon atoms, contains 60 per cent. of *l*-menthone and 40 per cent. of *d*-*iso*menthone (compare Beckmann, *Ber.*, 1909, **42**, 846).

It therefore appeared probable to the present author that Dakin's *iso*amygdalin contains a slight preponderance of the bioside of *d*-mandelonitrile. Moreover, since it possessed such poor powers of crystallisation, and melted indefinitely at relatively so low a temperature (125—140°), it was concluded that it did not consist chiefly of a definite, partially racemic compound, but was merely a mixture of isomerides. It was considered probable, therefore, that *iso*amygdalin would be capable of separation into its components, namely, amygdalin and the corresponding derivative of *d*-mandelonitrile—which is unknown—provided that it could be fractionally crystallised.

As, however, *iso*amygdalin itself cannot be fractionally crystallised in a satisfactory manner, its acetyl derivative has been selected as being a compound more suitable for effecting this resolution.

*iso*Amygdalin was therefore acetylated, and from the resulting product there have been separated, without much difficulty, hepta-acetylamygdalin and the hepta-acetyl derivative of the unknown isomeride of amygdalin. It is proposed to designate the latter neo*amygdalin*. *Hepta-acetyl*neo*amygdalin* has $[\alpha]_D$ $-65·6°$ in chloroform, and forms long needles, melting at 174°. On hydrolysis with concentrated hydrochloric acid it yields *d*-mandelic acid. All three varieties of mandelic acid may therefore be obtained from amygdalin.

Caldwell and Courtauld (Trans., 1907, **91**, 675) obtained from *iso*amygdalin a product which they regarded as hepta-acetyl*iso*amygdalin, although stating that its rotation differed but little from that of hepta-acetylamygdalin. Now, since amygdalin and *iso*amygdalin differ only stereochemically, and the biose radicle, which alone undergoes acetylation, is identical in both compounds, it follows that, if such a definite compound as hepta-acetyl*iso*amygdalin existed, its rotation would bear approximately the same relation to that of *iso*amygdalin as the rotation of hepta-acetylamygdalin does to that of amygdalin. This conclusion is substantiated by the results recorded in the present paper. It is evident, therefore, that Caldwell and Courtauld's "hepta-acetyl*iso*amygdalin" was only somewhat impure hepta-acetylamygdalin, and, by obtaining it, they afforded proof that the resolution of hepta-acetyl*iso*amygdalin was possible.

It does not appear feasible to regenerate *neo*amygdalin from its acetyl derivative, for, when treated with alkalis the latter is racemised, and when the acetyl groups are removed by mineral acids dextrose is also liberated.

EXPERIMENTAL.

The amygdalin employed was obtained from Kahlbaum. After drying for a short time at 120°, it melted at about 220°, when heated somewhat rapidly. The temperature at which fusion occurs, however, depends entirely on the rate of heating:

0·4054, made up to 20 c.c. with water, gave a_D $-1°32'$ in a 2-dcm. tube, whence $[a]_D$ $-37·8°$.

The material was twice recrystallised from dilute alcohol, and then dried for two hours at 120°, when the weight was constant, no appreciable change in colour occurring:

0·4247, made up to 20 c.c. with water, gave a_D $-1°37'$ in a 2-dcm. tube, whence $[a]_D$ $-38·0°$.

The rotation of *iso*amygdalin was determined by dissolving 0·4597 of anhydrous amygdalin in 20 c.c. of water containing a little ammonia. After standing overnight this solution gave a_D $-2°25'$ in a 2-dcm. tube, whence $[a]_D$ $-52·6°$. These values for the specific rotations of amygdalin and *iso*amygdalin, $-38·0°$ and $-52·6°$ respectively, are somewhat higher than those given by Caldwell and Courtauld (*loc. cit.*) for these substances ($-35·5°$ and $-47·6°$ respectively), but the latter figures probably refer to the hydrated material.

Before conducting experiments with hepta-acetyl*iso*amygdalin, a quantity of amygdalin was acetylated for the purpose of comparison. It is stated by the above-mentioned authors that hydrated amygdalin may be completely acetylated by boiling it for two hours with ten times its weight of acetic anhydride. The following method of preparing hepta-acetylamygdalin is, however, much more rapid and convenient.

Amygdalin was heated with an excess of acetic anhydride, and a trace of *d*-camphorsulphonic acid added (A. Reychler, *Bull. Soc. chim. Belg.*, 1907, **21**, 428). A vigorous reaction then takes place and the mixture boils spontaneously, acetylation being complete in about one minute. The greater part of the anhydride was then removed by distillation, and the residue diluted with about five times its volume of ether. Pure hepta-acetylamygdalin separates immediately, and the yield is almost quantitative. The product thus obtained melted at 166—167°, and, when recrystallised from alcohol, formed long, glistening needles:

0·4074, make up to 20 c.c. with chloroform, gave a_D $-1°32'$ in a 2-dcm. tube, whence $[a]_D$ $-37·6°$.

0·4065, made up to 20 c.c. with ethyl acetate, gave a_D $-1°23'$ in a 2-dcm. tube, whence $[a]_D$ $-34·0°$.

Acetylation of iso*Amygdalin. Separation of Hepta-acetylamygdalin.*

A few grams of amygdalin were dissolved in water, a little ammonia added, and the mixture allowed to stand overnight. The solution was then evaporated on the water-bath to a syrup, and the residue boiled for a short time with a large excess of acetic anhydride, a trace of *d*-camphorsulphonic acid having been added. After concentrating the solution to a small bulk, it was diluted with ether and cooled. As crystallisation did not begin quickly, this was initiated by means of a trace of hepta-acetylamygdalin. After about three hours the crystals were collected and washed with ether, when they melted at 159—160°. The yield was about 20 per cent. of that theoretically possible:

0·3400, made up to 20 c.c. with chloroform, gave α_D $-1°24'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-41·2°$.

After three crystallisations from alcohol the material melted at 166—167°, and was evidently pure hepta-acetylamygdalin, since the melting point was not lowered on mixing with an authentic specimen of the latter. A determination of the specific rotatory power gave the the following result:

0·4030, made up to 20 c.c. with chloroform, gave α_D $-1°31'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-37·6°$.

The above experiments were repeated several times, and were always attended with a similar result.

*Separation of Hepta-acetyl*neo*amygdalin.*

Twenty grams of amygdalin were converted into *iso*amygdalin by means of ammonia, and the product acetylated as described above. After removing the greater part of the anhydride by distillation, some alcohol was added, and the mixture largely diluted with ether. The solution was then brought into a separator and washed with water, when, as the alcohol was removed, a quantity of heavy, oily material was deposited from the ether, and was separated with the water. This oil became solid on standing, but the greater part of it could not be crystallised; some hepta-acetylamygdalin was, however, separated from it. On keeping the ethereal solution overnight, a quantity (about 9 grams) of crystalline material separated. This was recrystallised from alcohol, after which it melted at 168—172°, but when mixed with hepta-acetylamygdalin fusion occurred at 155—158°. The substance was evidently fully acetylated, for it was not changed by prolonged treatment with acetic anhydride:

0·4027, made up to 20 c.c. with chloroform, gave α_D $-2°34'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-63·7°$.

By successive crystallisations from alcohol the melting point and rotation of this preparation were at first slowly raised, but after the fifth crystallisation no further change was effected. The compound then melted sharply at 174°, but when mixed with hepta-acetylamygdalin fusion occurred at 155—157° :

0·1897 gave 0·3750 CO_2 and 0·0975 H_2O. C = 53·9 ; H = 5·7.

$C_{34}H_{41}O_{18}N$ requires C = 54·3 ; H = 5·5 per cent.

0·4422, made up to 20 c.c. with chloroform, gave a_D $-2°54'$ in a 2-dcm. tube, whence $[a]_D$ $-65·6°$.

0·4436, made up to 20 c.c. with ethyl acetate, gave a_D $-2°32'$ in a 2-dcm. tube, whence $[a]_D$ $-57·1°$.

*Hepta-acetyl*neo*amygdalin* crystallised in long, colourless needles, which are more slender than those yielded by hepta-acetylamygdalin. It is readily soluble in chloroform or ethyl acetate, but somewhat sparingly so in alcohol.

*Hydrolysis of Hepta-acetyl*neo*amygdalin. Formation of* d-*Mandelic Acid.*

As the change from amygdalin to *iso*amygdalin involves the racemisation of the mandelonitrile part of the molecule, *neo*amygdalin should yield *d*-mandelic acid on hydrolysis with concentrated hydrochloric acid, just as amygdalin yields the lævo-isomeride. A quantity of hepta-acetyl*neo*amygdalin was, therefore, boiled for three hours with a mixture of concentrated hydrochloric acid and alcohol. At the end of this time the solution, which had become very dark in colour, was treated with animal charcoal, after which it was extracted many times with ether. The residue obtained on removing the ether was crystallised from benzene, when highly lustrous leaflets were obtained which melted at 132—133° :

0·1038, made up to 20 c.c. with water, gave a_D $+1°34'$ in a 2-dcm. tube, whence $[a]_D$ $+151·1°$.

The above substance was evidently nearly pure *d*-mandelic acid. When mixed with *l*-mandelic acid prepared from amygdalin, *i*-mandelic acid (m. p. 118°) was obtained.

*iso*Amygdalin and amygdalinic acid respectively consist of mixtures of stereoisomerides, but, for reasons stated in the introductory portion of this paper, it was concluded that the latter would not necessarily occur in equal proportions. In order to ascertain whether this was the case, each of the two compounds in question was hydrolysed by means of hydrochloric acid. It was then found, in agreement with the observations of Dakin (*loc. cit.*), that whilst the mandelic acid yielded by amygdalinic acid was inactive, that obtained from *iso*amygdalin invariably possessed a slight dextro-rotation. It appears, therefore, that amygdalinic acid consists of a mixture of equal proportions of the biosides of *d*- and *l*-mandelic acids respectively, whilst *iso*amygdalin is a mixture of amygdalin and *neo*amygdalin, the latter slightly predominating. The specific rotation of *iso*amygdalin (−52·6°) must therefore be greater than the mean of the corresponding values for amygdalin and *neo*amygdalin, and consequently the latter compound, when anhydrous, will have a specific rotation somewhat less than −67·0°.

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LXXXI.—*The Miscibility of the Pyridine Bases with Water and the Influence of a Critical-solution Point on the Shape of the Melting-point Curve.*

By OTTO FLASCHNER.

A PREVIOUS investigation (Flaschner, *Zeitsch. physikal. Chem.*, 1908, **62**, 493; Flaschner and McEwen, Trans., 1908, **93**, 1000) on the mutual solubility of some bases of the pyridine and piperidine series and water has shown that the introduction of a methyl group decreases the solubility. This influence is strongest when the methyl group is attached to the nitrogen atom; thus 1-methylpiperidine has a lower critical-solution temperature of 48·3°, and the data point to the existence of an upper one of about 290°; 2-methylpiperidine forms with water a complete solubility ring between 79·3° and 227°. In the present paper the attempt to determine the solubility of the β- and γ-substituted homologues is described.

The physical properties of these substances as determined by previous observers are not in good agreement. γ-Picoline is usually isolated from the mixture of pyridine bases as the fraction 143—146°, and is then converted into the mercury double salt, which is recrystallised. Ladenburg (*Annalen*, 1888, **247**, 11) heated pyridine methiodide to 300° and fractionated the products of the reaction. β-Picoline can be isolated in small quantities from bone oil or from the mixture obtained by heating glycerol with ammonium phosphate and phosphoric oxide (Ladenburg, *Ber.*, 1890, **23**, 2688; Stöhr, *J. pr. Chem.*, 1892, [ii], **45**, 23), or ammonium sulphate and sulphuric acid (Storch, *Ber.*, 1886, **19**, 2458). Marcuse and

Wolffenstein (*Ber.*, 1899, **32**, 2526) removed the α-picoline by converting it into its aldehyde condensation product. It is evident that there is no practicable method of synthesising one of the homologues, as these always occur mixed together, and cannot be completely separated. As will be pointed out later, the recrystallisation of the mercury double salt does not improve the purity of the product much, even if one employs the following strange method described by Constam and White (*Amer. Chem. J.*, 1903, **29**, 1): "On account of the number of impurities present, all of which form difficultly soluble chlorides with mercury, differing very little in point of solubility from that of the β-salt, the crystallisation had to be controlled by means of the magnifying glass, and only when an absolutely uniform product was obtained were we satisfied as to its purity." I have now found that all these homologues are isomorphous, and therefore form mixed crystals, the composition of which even Constam and White could hardly detect by means of a lens. It seems far more advisable to adopt a process of purification by determining a physical constant.

The initial material employed in this research was 800 grams of so-called β-picoline (Schuchardt). This was fractionated with a Young's three-chamber "evaporator" fractionating column, fractions being collected between 126° and 160°, first at intervals of 1° and finally of 0·25° until further fractionation did not change the weights of the single fractions. This stage was reached after eight fractionations. The main part distilled at the following temperatures:

143·75—144·00°	22·5 grams.	144·75—145·00°	51·3 grams.
144·00—144·25	29·3 ,,	145·00—145·25	46·6 ,,
144·25—144·5	46·8 ,,	145·25—145·5	24·2 ,,
144·5 —144·75	59·5 ,,		

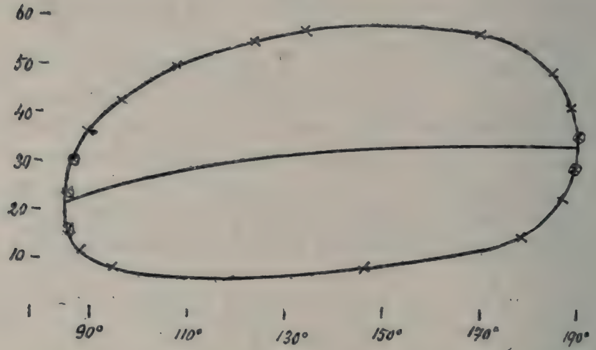
The fractions 144·25° to 145·25° were again united and a part was transformed into the mercury double salt. This was recrystallised four times from water and then decomposed with potassium hydroxide. The free base was now fractionated. The mother liquors were united, the base set free, and fractionated as well. The result was that neither in the recrystallised product nor in the mother liquor was a substance of constant boiling point accumulated. It is therefore impossible to obtain a reasonable purification by employing the mercury salt, which hitherto has always been used in such cases. In view of the greater differences between the melting points of the zinc double salts, the attempt was now made to use these as a means of purification of the basic mixture. An amount of zinc chloride greater by one half than that required for the combination was dissolved in water, the solution filtered, and poured into a cooled solution of the base in water (1 : 5). The zinc salt was precipitated and recrystallised twice from alcohol. Water cannot be used, because it dissolves the salt sparingly and causes loss by hydrolysing the salt at higher temperatures to a great extent.

The recrystallised zinc salt was decomposed and the base fractionated. It boiled constantly at 145·05°. The base was again transformed into the zinc salt and recrystallised three times; it was then isolated and fractionated. It distilled completely at 145·08°, showing that the substance thus obtained was pure.

The boiling point of γ-picoline given by different observers varies between 142·5° and 144·5°. It was concluded from the solubility in water that the substance obtained was γ-picoline. The purity of the product is proved by (1) the constancy of its boiling point, and (2) the modified method of Crismer explained later on.

The mother liquors of the zinc salts contained apparently β-picoline and 2 : 6-lutidine. By a combination of fractional crystallisation of the zinc salt and fractional distillation of the free bases, I was able to separate two products. The first boiled at 143·2° and was very probably 2 : 6-lutidine. The second, which boiled at 143·9°, was present in greater quantity and was regarded as β-picoline. Although the purity of both substances was far from being so satisfactory as that of γ-picoline, determinations of their solubilities were made in view of the fact that these are very nearly equal.

FIG. 1.



The β- and γ-picolines were reduced in alcoholic solution with sodium and the products were purified by fractionation.

The solubility of these bases in water was determined by Alexéeff's method. In the case of the reduced bases, the operation was carried out in Jena-glass tubes. The percentage compositions of the mixtures by weight are as follows.

4-*Methylpiperidine and Water* (Fig. 1).

Percentage of base.	Lower solution-point.	Upper solution-point.	Percentage of base.	Lower solution-point.	Upper solution-point.
57·5	133·0°	168·5°	30·0	85·9°†	188·8°†
55·0	122·7	—	23·7	84·9*	186·2
49·4	106·9	183·6	16·0	85·1†	178·0
42·4	95·5	187·5	11·6	87·6	157·8
36·2	88·8	189·5 *	8·9	94·2	146·0

* Strong critical opalescence.

† Critical opalescence. The points where critical opalescence was visible are marked in the diagram by small rings.

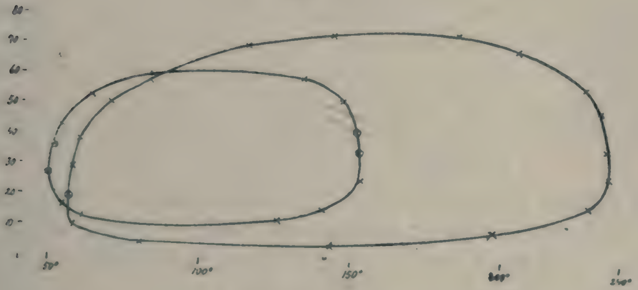
The purity of the substance was tested by Crismer's method, which consists in determining the critical-solution points of the first fraction :

29·9	89·4°	184·5°

and the last fraction :

29·7	86·5°	187·6°

FIG. 2.



Considering that with the small amount of 4-methylpiperidine (b. p. 126°) available a complete separation from picoline (b. p. 145·08°) is impossible, the result of the test is satisfactory. Using larger quantities, however, it might be worth while precipitating the picoline with mercuric chloride in order to separate it from the reduced base.

β-Picoline and Water.

Percentage of picoline.	Lower solution-point.	Upper solution-point.	Percentage of picoline.	Lower solution-point.	Upper solution-point.
59·7	83·5°	133·3°	26·4	49·4°*	152·5°
52·3	63·3	146·5	16·4	54·5	140·0
42·3	53·7	151·0*	12·7	61·0	125·7
35·5	51·4*	152·0	9·7	homogeneous.	

* Critical opalescence.

These numbers are shown in Fig. 2 by the narrower ring.

3-*Methylpiperidine and Water.*

Percentage of 3-methyl-piperidine.	Lower solution-point.	Upper solution-point.
74·8	142·2°	184·0°
70·1	115·0	204·0
58·2	82·0	226·5
50·5	69·8	232·0
38·1	59·9	234·0
29·2	57·5°	235·0°
19·2	56·9	228·5
9·9	58·1	197·0
4·8	80·0	143·0

Represented by the wide ring in Fig. 2.

2 : 6-*Lutidine and Water*

Percentage of 2 : 6-lutidine.	Lower solution-point.	Upper solution-point.
79·1	homogeneous.	
66·9	92·2°	130·5°
54·8	59·3	157·0
46·4	50·2	161·6*
40·6	47·7	163·4*
33·8	45·4°*	164·9°
27·2	45·3	164·0
18·1	48·1	153·5
12·1	57·7	132·7
9·5	74·5	105·0

* Critical opalescence.

First fraction :

30·2 49·3° 162·7°

Last fraction :

28·7 47·4° 162·4°

The lutidine boiled at 143·2°. As can be seen from the last figures, it was contaminated with substances of lower and higher boiling points respectively, both of which are more soluble than itself, namely, α- and β-picoline. The miscibility of 2 : 6-lutidine with water is represented by a closed curve with a lower critical temperature of about 45° and an upper one of 163·5. As it does not differ in shape from the other ones, no diagram is given.

Discussing the question how the solubility is influenced by chemical constitution, one can only expect regularities if one does not depend on the accidental position of the temperature of experiment. This is avoided by determining the mutual solubility as far as the critical-solution point. The distance between the lower and upper critical-solution points, that is, the width of the solubility ring, gives a comparable measure of the miscibility of two liquids. Of course it will often occur that the lower critical-solution point cannot be reached on account of the appearance of a solid phase, whilst the upper critical-solution point may lay higher than the critical-evaporation point of one or other of the liquid layers (Büchner, *Zeitsch. physikal. Chem.*, 1906, **56**, 267 ; Kuenen and Robson, *Zeitsch. physikal.*

Chem., 1894, **28**, 345). Addition of a third substance affords a means of bringing the critical solution-temperature into a region, where it can be measured. By extrapolating, we can easily determine the critical-solution temperature of the pure substance, which is otherwise not accessible. On the other hand, it will often occur that the mutual solubility of two liquids at all temperatures is complete. What is the measure for the miscibility of such liquids?

Timmermans has recently published a paper (*Bull. Soc. chim. Belg.*, 1909, **23**, 129) in which he again draws attention to the influence of the external pressure on the critical-solution point, and concludes that two partially miscible liquids, when exposed to a certain pressure, will become completely miscible. Timmermans calls this point in the pressure-concentration-temperature diagram, according to Büchner's nomenclature, a terminal critical-solution point (kritischer Lösungsendpunkt). If we consider the mutual solubility in the neighbourhood of such a terminal critical point, we see that increase of pressure will cause a rise of the lower and a fall of the upper critical-solution point, that is, shrinking of the solubility ring. The following cases have hitherto been observed: Kuenen (*Phil. Mag.*, 1903, [vi], **6**, 637) found that between 1 and 100 atmospheres an increase of pressure of 1 atmosphere depresses the upper critical-solution point of the system propane–methyl alcohol by 0·044° and raises the lower critical-solution temperature of the system triethylamine–water by 0·021°. By studying the influence of increasing pressure on a system with very small solubility ring, as, for example, 4-methylpiperidine and water, one could determine the alteration of both critical-solution temperatures on the same system. The solubility ring of such a system is only the section of the p,c,t diagram, for $p_c = 1$ atm. If we increase the pressure, we reach a certain point—the terminal critical-solution point—where the upper and lower critical-solution temperatures become identical, that is, the solubility ring shrinks to a single point which is completely determined with regard to pressure, temperature, and concentration. At that point the system becomes completely miscible. By further increasing the pressure, we are not able to detect any difference in the miscibility, which has already become complete. A pair of completely miscible liquids, such as γ-picoline and water, shows at normal pressure the same behaviour as 4-methylpiperidine and water when exposed to a pressure slightly higher than the terminal pressure. If we now relieve this pressure, or if we exert a negative pressure, opalescence will be observed, owing to the formation of two liquid phases. This diminution of pressure, which may be called the "separation pressure" (Entmischungsdruck), is characteristic of the miscibility of a pair of liquids which are completely miscible under normal pressure. The separation-pressure of the system pyridine–water is far greater than that of the system γ-picoline–water. In the majority of cases, however, it will prove impossible to reach a sufficiently high negative pressure to cause separation. It is therefore necessary to introduce into our definition of the "separation pressure" a magnitude which can easily be determined experimentally. Such a one is the concentration of a third substance added to the system. Timmermans (*Zeitsch. physikal. Chem.*, 1907, **58**, 129) has studied the influence of added substances on the critical-solution point, and has found that substances soluble to the same extent in both liquids increase the mutual solubility, that is, they have the same effect as increased pressure in the example given above. Substances soluble only in one of the two liquids decrease the mutual solubility, that is, they act like decreased pressure. Tammann has pointed out that liquids exposed to an external pressure show an analogous behaviour to solutions, that is, liquids the internal pressure of which is increased by dissolving in them a second substance. Tammann ("*Beziehungen zwischen den inneren Kräften, etc.,*" p. 183) himself drew attention to the fact that a gas may be expelled from a liquid by dissolving a salt in it. Ritzel (*Zeitsch. physikal. Chem.*, 1907, **60**, 319) has shown that the solubility of an indifferent gas in organic solvents is directly proportional to the compressibility of the liquid. But since the compressibility of solution of salts is smaller than that of the solvent, a less solubility of the gas is to be expected. Similar considerations follow if one employs, instead of a gas, a second liquid, which does not dissolve the salt added. A salt dissolved in a mixture of two liquids will therefore cause an increase of the internal pressure of the one liquid and so force the other out, that is, it will have the same effect as exerting an external pressure by means of a semipermeable pressure piston, or in the case discussed above, as a decrease of external pressure. A salt which is equally soluble in both liquids will increase the mutual attraction of the liquid molecules, that is, it will increase the mutual solubility or have the same effect as increase of the pressure in the above case.

There are systems known in which an increased pressure raises the upper critical-solution point (van der Lee, *Zeitsch. physikal. Chem.*, 1900, **33**, 622; Kuenen, *loc. cit.*). They are very far from the terminal critical pressure—if they belong to the same class of systems at all—and are not included in the above considerations.

As there is such a close connexion between the influence of a dissolved third substance and that of external pressure, it may be sufficient to determine the numerical relation between small pressures and dissolved substances, and then to carry on the experiments with the latter until separation into two liquid layers takes place. The concentration of a salt (or third substance) which just effects liquid separation in the critical region at normal pressure corresponds with the "separation pressure" and may be called "separation concentration."

For practical purposes of comparison it may be more convenient, instead of using the term separation concentration, to speak of the width of that solubility ring which, starting from the terminal critical point, is reached by the same concentration of salt as the terminal point itself. This ring may be called the "characteristic negative ring," because it lies as far behind the terminal critical point as the normal pressure lies in front of it. The characteristic negative ring is thus the ring which shrinks into a single point under the separation pressure. Such negative rings afford a comparable measure for the miscibility of completely miscible liquids.

For the experimental determination of the characteristic negative ring, it is in the first place necessary to salt out different mixtures of the two liquids and select that concentration as critical which is accompanied by the strongest critical opalescence. Then one determines for that special concentration the lower and upper critical-solution temperature, adding two or three different quantities of salt, and connects these points in a *t,c* diagram by a parabolic curve. The concentration which corresponds with the vertex of the curve is the separation concentration. The solubility ring which is obtained when the concentration is twice as great as the separation concentration is the characteristic negative solubility ring.

Values for the negative rings of some pairs of completely miscible liquids will now be given.

Pyridine and Water.[*]

The critical concentration was first determined and was found to be about 34·6 per cent. of the base. A solution of this strength shows a strong critical opalescence in the neighbourhood of the upper and lower critical-solution points if a salt like potassium chloride is added.

Percentage of potassium chloride.	Lower critical-solution point.	Upper critical-solution point.
8·9	93·0°	130·0°
10·2	59·4	180·4

If one therefore adds to an aqueous solution containing 34·6 per cent. of pyridine 8·7 per cent. of potassium chloride, one just reaches the limit where the two liquids become miscible in all proportions, and, on the other hand, a further trace of salt effects separation into two

[*] I am indebted to Mr. Rankin for making this determination.

layers. The characteristic ring corresponding with 17·4 per cent. of potassium chloride in this case can only be extrapolated and is about 340°.

Piperidine and Water.

The critical concentration is about 33·3 per cent. of the base. The negative ring had previously (*Zeitsch. physikal. Chem.*, 1908, **62**, 494) been determined on the assumption that the change of the critical-solution temperature is proportional to the amount of salt added. As this is not correct in the immediate neighbourhood of the terminal point, the ring had to be recalculated.

Percentage of potassium chloride.		
3·7	Homogeneous solution.	
3·9	155·2°	200°
5·0	123·5	258

The separation concentration is 3·75 per cent. of potassium chloride; the characteristic ring about 240° (90—330).

a-Picoline and Water.

The critical concentration is 29·6 per cent. of the base.

Percentage of potassium chloride.		
0·6	104·0°	112·7°
1·0	84·4	131·7
1·5	68·8	155·4

The separation concentration is 0·56 per cent. of potassium chloride; the characteristic ring corresponding with 1·12 per cent. of potassium chloride lies between 77·5° and 142°, and has thus a width of 64·5°. See Fig. 3.

γ-Picoline and Water.

The critical concentration is 31 per cent. of the base.

Percentage of potassium chloride.		
0·54	Homogeneous solution.	
1·0	65·8°	100·6°
1·5	47·3	126·1
2·1	37·3	143·0

These numbers are shown in Fig. 4.

The terminal critical point is 82·5°, corresponding with 0·86 per cent. of potassium chloride. The characteristic ring lies between 43° and 133·5°, and has thus a width of 90·5°.

The Modified Method of Crismer.

Crismer's method for testing the purity of a liquid consists in the determination of the critical-solution point of the single fractions. The general use of this method has hitherto been limited for lack of a second liquid, which gives with the liquid to be tested an easily accessible critical-solution point. The difficulty may be overcome by employing solutions instead of pure liquids. In the present case, the purity of γ-picoline was examined. The critical concentration of the middle fraction was first determined by observing the strength of the critical opalescence, and was found to be 31 per cent. of the base. The shape of the critical zone was next determined in the manner described, and was marked in Fig. 4 by points. Then two points of the critical zone were determined, employing the first fraction as one liquid, and an aqueous solution of potassium chloride as the other.

FIG. 3.

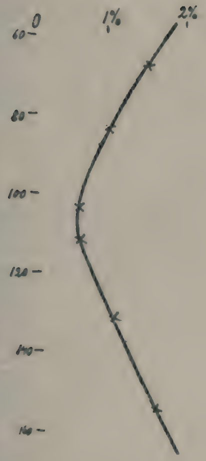
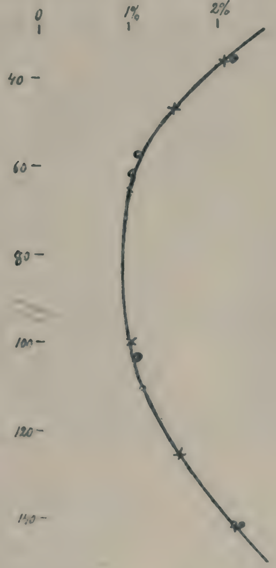


FIG 4.



Percentage of potassium chloride.		
0·0	Homogeneous solution.	
1·1	57·4°	111·1°
2·1	37·8	142·2

In the same way, two points with the last fraction were determined:

1·04	62·8°	103·9°
2·16	37·6	142·8

The points of the first fraction are marked in the figure as small rings, the points of the last fraction as ⊙. If the liquid is quite pure, all these points must lie on the same curve. It can be seen from the figure that the γ-picoline was of a high degree of purity.

The method is also available for a pair of liquids which are too little miscible at the ordinary temperature if one adds a third substance which is almost equally soluble in both liquids.

Nitrosopiperidine and Water.

As nitrosopiperidine can easily be obtained, I determined its solubility with water.

Percentage of nitroso-piperidine.	Upper solution-point.	Lower solution-point.
94·6	31·5°	—
85·9	103·5	—
75·6	133·4	—
67·0	143·5	—
58·9	147·7	—
51·9	149·3	—
43·3	150·3°	—
38·5	150·3	—
30·1	148·0	—
22·7	141·5	—
15·2	124·0	—
8·1	73·5	14·5°

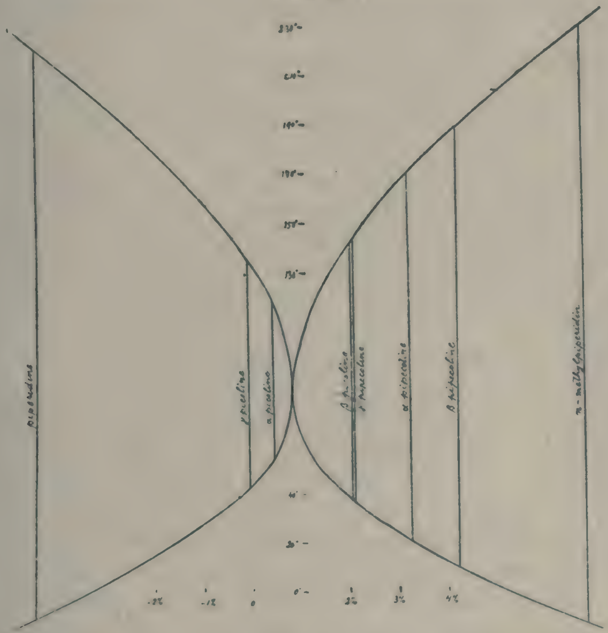
The upper critical-solution temperature is 150·3°; the critical concentration 43 per cent.; the centre of the solubility ring is about 15°. Introduction of a nitroso-group attached to the basic nitrogen atom greatly decreases the solubility.

The results obtained are collected below:

			Per cent. KCl.
Pyridine + water	negative ring, 340·0°	Separation concentration	8·7
α-Picoline + water	,, ,, 64·5	,, ,,	0·56
β-Picoline + water	positive ring, 103·0	—	—
γ-Picoline + water	negative ring, 90·5	Separation concentration	0·86
Piperidine + water	,, ,, 240·0	,, ,,	3·75
1-Methylpiperidine + water.	positive ring, 242·0	—	—
2-Methylpiperidine + water.	,, ,, 148·0	—	—
3-Methylpiperidine + water.	,, ,, 178·1	—	—
4-Methylpiperidine + water.	,, ,, 104·6	—	—

A convenient survey of the mutual solubilities of different members of a homologous series can be obtained if one determines first for one homologue, as, for example, γ-picoline and water, the critical zone by adding different amounts of a third salt. It is convenient to take a homologue which requires a very small separation concentration of salt. Now, in the vertex of the parabolic curve, the mirror of that curve is constructed as shown in Fig. 5. In the left part of the mirror the homologues with a negative solubility ring are drawn as ordinates at such a distance from the vertex as the separating concentration indicates. In the right part of the mirror the width of the solubility rings are drawn at such a distance that they just fit the curve. The distances between these lines are differences in concentration of the third substance, and can easily be expressed in atmospheres of external pressure if the ratio is known. They are a direct measure of the mutual solubility of the members of the homologous series. The method is so far not quite correct, as the centres of the different rings are often shifted.

FIG. 5.



From Fig. 5 it is evident that the methyl group has the greatest influence when attached to the nitrogen, then follow the 2-, 3-, and 4-positions in the series of pyridines and their reduction products.

The Melting-point Curve in the Neighbourhood of a Critical-solution Point.

In the majority of cases the shape of the melting-point curve is well expressed by the equation (van't Hoff, *Kongl. Svenska Akad. Handl.*, 1886, **21**, 17; Le Chatelier, *Compt. rend.*, 1885, **100**, 441; T. Schröder, *Zeitsch. physikal Chem.*, 1893, **11**, 449):

$$\frac{d\ln\eta}{dT} = \frac{Q}{RT^2},$$

η expressing the volume concentration and Q the heat of solution. This equation does not show an inflexion point. A more general equation is deduced by Rothmund (*Löslichkeit*, p. 50), following van der Waals:

$$\frac{dlnc}{dT} = -\frac{Q}{RT^2(1-c)\left(\frac{dlnp}{dc}\right)_T},$$

where c means the mass solubility and p the vapour pressure. By this equation we can discuss the results found in the present case. If $\frac{dlnp}{dc}$ is very small, then $\frac{dlnc}{dT}$ becomes very large, that is, the melting-point curve will ascend very steeply. If $\frac{dlnp}{dc}=0$, the melting-point curve at that point is vertical. If $\frac{dlnp}{ac}$ becomes positive, the concentration will decrease if the temperature rises. In reality the partial pressure cannot rise when the concentration of an added substance increases. Also, the vapour pressure of a gas cannot decrease when the volume decreases. But as in the latter case condensation takes place, so in the former, separation of a second liquid layer will be observed. Van Laar (*Zeitsch. physikal. Chem.*, 1908, **63**, 216), employing the idea of thermodynamical potential, has deduced a quite general formula which embraces a region of solid as well as liquid separation. In all the cases, however, where liquid separation into two layers is observed, the range of miscibility in the solid phases is exceedingly small and, as in our case, practically vanishes. Van Laar (*Zeitsch. physikal. Chem.*, 1908, **64**, 274) has now shown by his equation that if the melting-point curve shows a vertical inflexion point, this point must be identical with the critical-solution point. This case nearly occurs in the system γ-picoline zincichloride–octyl alcohol. If the critical-solution temperature rises, the melting-point curve is cut by the solubility curve, that is, the substance melts below the solution: above zinc salt + water, above zinc salt + hexadecyl alcohol. If the critical-solution point is low, its neighbourhood is shown by a more or less steep sloping of the melting-point curve: above zinc salt + methyl to amyl alcohol. The same change of the shape of the melting-point curve is observed in the neighbourhood of an upper critical-solution point: salicylic acid and water (Alexéeff, *Wied. Annalen*, 1886, **28**, 330), potassium salt of trinitrophenylnitramine and water (Roozeboom, *Rec. trav. chim.*, 1889, **8**, 2); in the neighbourhood of a lower critical-solution point: nitrobenzene and carbon dioxide, *o*-nitrophenol and carbon dioxide, and *m*-chloro-phenol and carbon dioxide (Büchner, *Zeitsch. physikal. Chem.*, 1906, **54**, 665).

The same is to be expected with the melting-point curves of the homologues of the pyridine series. Fusion below the solution in the neighbourhood of an upper critical-solution point has hitherto been observed in the following cases: benzoic acid and water (Alexéeff, *Wied. Annalen*, 1886, **28**, 330), resorcinol and benzene (Rothmund, *Zeitsch. physikal. Chem.*, 1894, **26**, 433), succinonitrile and water (Schreinemakers, *Zeitsch. physikal. Chem.*, 1897, **23**, 418), phenol and water, *p*-toluidine and water (Walker, *Zeitsch. physikal. Chem.*, 1892, **5**, 190), thallium and aluminium (or copper) (Doerinckel, *Zeitsch. anorg. Chem.*, 1906, **48**, 184), sodium and aluminium (magnesium) (Matthewson, *Zeitsch. anorg. Chem.*, 1902, **48**, 192), bismuth and aluminium (Gwyer, *Zeitsch. anorg. Chem.*, 1906, **49**, 311).

Fusion below the solution in the neighbourhood of a lower critical-solution point, which then lies in the metastable or unstable field, has been observed for: *o*-bromonitrobenzene and carbon dioxide, dichloronitrobenzene and carbon dioxide, urethane and carbon dioxide, *m*-chloronitrobenzene and carbon dioxide (Büchner, *loc. cit.*), and pyridinium methiodide and pyridine (Aten, *Zeitsch. physikal. Chem.*, 1905, **54**, 124).

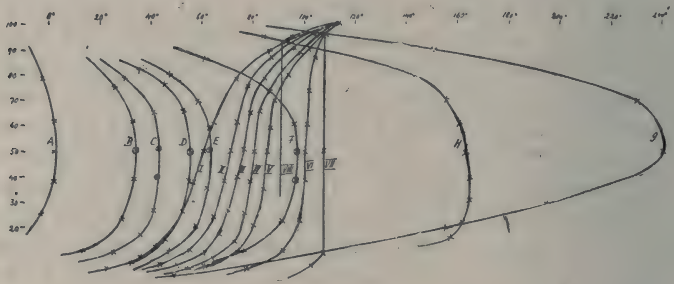
On recrystallising γ-picoline zincichloride from alcohol it was found that by quickly cooling the solution the zinc salt was separated out of solution as a second liquid layer. On the other hand, the somewhat cooled liquid was found to be supersaturated with regard to solid crystals. It appeared therefore evident that the same kind of system was present as was first observed in the case of salicylic acid and water. For reasons shown above, it seemed of interest to determine the shape of the melting-point curve as well as that of the solubility curve, which here lies, of course, in the metastable zone. These curves were therefore determined for the first members of the series of aliphatic alcohols, water and benzyl alcohol. The method was as follows: A certain mixture of solid zinc salt and alcohol contained in a small glass tube was heated in a sulphuric acid bath until the last crystal vanished. Thus a rough value of the melting point was obtained. Then the temperature was allowed to fall a little, but not so far as the critical-solution temperature. A tiny crystal was now thrown into the solution and the tube was constantly shaken, so that from the supercooled solution crystals of quite a minute size separated out. Then the temperature was very slowly raised, the tube being constantly shaken. The temperature at which the last crystal vanished was regarded as the melting point. I found that the results obtained by this method were sufficiently accurate. The bath was finally cooled down, and the temperature determined at which separation into two liquid layers took place.

γ-Picoline Zincichloride and Methyl Alcohol.

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
89·0	86·4°	—	37·9	56·7°	+1·1°
78·5	73·5	−3·0°	25·2	52·0	−3·5
61 5	64·2	+1·5	12·7	41·5	—
49·7	60·5	+1·9	6·0	31·5	—

The critical point of the solubility curve lies at +1·9° for a concentration of 50 per cent. Although the distance of that point from the melting-point curve is about 60°, the liquid separation has already a considerable influence on the shape of the melting-point curve, which shows clearly a point of inflexion. In Fig. 6, the solubility curve is marked *A*, the melting-point curve, *I*.

FIG. 6.



γ-Picoline Zincichloride and Ethyl Alcohol † (*B* and *II in* Fig. 6).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
86·9	88·7°	—	38·5	68·5°	32·9°*
75·5	78·8	25·5°	23·8	64·5	28·4
61·6	73·1	32·4	10·7	55·0	12·8
50·2	71·0	33·4*	5·0	43·5	—

* Critical opalescence.

† The alcohol was absolute and prepared by Sydney Young's method.

γ-Picoline Zincichloride and n-*Propyl Alcohol* (*C* and *III* in Fig. 6).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
90·3	96·0°	—	26·6	70·2°	40·7°
78·3	84·0	29·2°	17·0	67·1	35·4
65·1	78·6	40·7	10·0	60·5	25·0
50·9	76·3	52·5*	5·0	50·0	—
39·7	73·8	42·0*			

* Critical opalescence.

γ-Picoline Zincichloride and iso*Butyl Alcohol* (b. p. 107·8°) (*D* and *IV*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
88·8	98·6°	—	37·9	78·4°	54·6°*
82·1	—	35·0°	25·9	76·7	52·1
76·3	87·5	44·7	14·9	72·5	45·4
65·5	82·7	52·3	8·0	64·3	35·6
49·5	80·0	55·0*	4·0	54·7	22·7

* Critical opalescence.

γ-Picoline Zincichloride and iso*Amyl Alcohol* (b. p. 131·5°) (*E* and *V*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
88·1	99·8°	—	35·0	83·9°	61·8°
80·0	93·7	46·5°	20·5	79·8	57·1
69·6	88·1	57·9	10·8	74·0	46·5
59·4	86·5	62·2	4·7	61·0	—
50·0	85·4	62·9*			

* Critical opalescence.

γ-Picoline Zincichloride and Methylhexylcarbinol (b. p. 179·5°). (*F* and *VI*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
86·2	104·0°	60·5°	38·2	100·0°	96·5°
73·5	101·8	86·6	22·2	97·7	91·1
60·1	100·3	95·8	10·7	91·7	76·0
49·4	100·2	97·0	3·8	77·0	—

The solubility and melting-point curves nearly touch each other, therefore the latter rises nearly vertically in the critical region.

γ-Picoline Zincichloride and Cetyl Alcohol (*G* and *VII*).*

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
95·8	108°	104°	20·0	—	155·0°
89·5	—	150	9·7	108·0°	120·6
69·7	—	230	4·9	102·5	92·0
50·0	108	241	1·0	54·0	48·0
30·0	—	195			

The alcohol used was purified as follows: It was dissolved in benzene, the solution was then cooled to 0°, and the crystals which formed were quickly collected, pressed between filter paper, and heated for some hours to 130°. On cooling, the pure alcohol crystallised out and melted at 48°. As seen in Fig. 6, the solubility curve cuts the melting-point curve. The zinc salt, therefore, below its alcoholic solution, melts constantly at 108°.

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* The determination of this pair was carried out by Mr. Rankin.

γ-Picoline Zincichloride and Water (*H* and *VIII*).

Percentage of salt.	Melting point.	Solution point.	Percentage of salt.	Melting point.	Solution point.
95·0	95°	84·0°	40·4	—	164·6°*
92·9	91	89·5	30·6	—	164·6
80·0	—	142·2	21·8	—	161·7
70·5	—	155·0	16·1	—	156·5
61·6	—	160·0	12·5	—	144·0
49·5	91	163·0*			

* Critical opalescence.

At higher concentrations of water an exact determination of the solubility point is impossible on account of the hydrolysis of the zinc salt. In this case, also, fusion below the solution takes place. It is surprising that the behaviour of water towards the zinc salt is similar to that of an aliphatic alcohol with about twelve carbon atoms, whereas one might expect that the solubility curve would lie below that of methyl alcohol. This exceptional position of water proves that a comparison of physical properties ought always to be restricted to members of the same homologous series.

γ-Picoline Zincichloride and Benzyl Alcohol.

Percentage of salt ...	90·0	76·7	62·9	50·4	39·3	26·3
Melting point	101·7°	86·7°	70·1°	57·1°	46·3°	34·0°

A 50 per cent. solution remains clear even on cooling to $-78°$; also, from the shape of the melting-point curve, which differs but little from a straight line, it is evident that it must lie very far above the solubility curve. It would rather have been expected that the parts played by water and benzyl alcohol would be reversed.

As the melting-point curve illustrates the change of the osmotic pressure in a solution, it is possible to give an account of the π,c curves in the neighbourhood of the critical-solution point. In a t,c diagram is drawn the melting-point and solubility curves of the two liquids which show the highest critical-solution point (γ-picoline zincichloride and cetyl alcohol). As the lower alcohols show an additive behaviour towards the higher ones, the melting-point curves of the different alcohols are comparable. Therefore the melting curves of the other members of the same series are drawn at the given distances from this critical point, as only this distance influences inflexion. In the following table are given the slopes of the melting-point curves in the critical region and the distance from the critical-solution point.

		Distance.	$\frac{dc}{dt}$.
Zinc salt and	methyl alcohol	58·6°	3·1
,,	ethyl alcohol	37·6	4·7
,,	*iso*butyl alcohol	25·0	7·3
,,	*iso*amyl alcohol	22·5	10·0
,,	methylhexylcarbinol	3·2	56·0

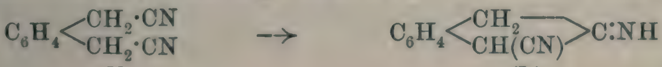
This research was carried out in the summer of 1908 in the chemical laboratory of Trinity College, Dublin. I wish to express my sincerest thanks to Prof. Sydney Young for his keen interest and advice, and for the facilities he placed at my disposal.

TRINITY COLLEGE, DUBLIN.

LXXXII.—*The Formation and Reactions of Imino-compounds. Part IX. The Formation of Derivatives of* cyclo*Pentane from aδ-Dicyano-derivatives of Butane.*

By STANLEY ROBERT BEST and JOCELYN FIELD THORPE.

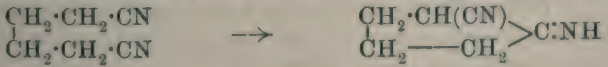
IN a former communication (Trans., 1908, **93**, 165) it was shown that *β*-imino-*a*-cyanohydrindene (I) can be obtained in practically quantitative yield on warming an alcoholic solution of *o*-phenylenediacetonitrile (II) containing a trace of sodium ethoxide, thus:



$$C_6H_4\Big<\begin{array}{l}CH_2\cdot CN\\CH_2\cdot CN\end{array} \longrightarrow C_6H_4\Big<\begin{array}{l}CH_2\text{——}\\CH(CN)\end{array}\Big>C{:}NH$$

(II.) (I.)

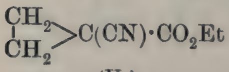
The ease with which the formation of the five-carbon ring took place in this instance gave rise to the idea that in all probability five-carbon alicyclic compounds would also be formed in like manner, that is to say, *aδ*-dicyanobutane (III) would, for example, on treatment with sodium ethoxide pass into 1-imino-2-cyano*cyclo*pentane (IV).



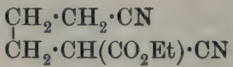
$$\begin{array}{l}CH_2\cdot CH_2\cdot CN\\|\\CH_2\cdot CH_2\cdot CN\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CH(CN)\\|\\CH_2\text{——}CH_2\end{array}\Big>C{:}NH$$

(III.) (IV.)

While experiments on the condition of formation of *aδ*-dicyanobutane were being instituted, the literature was searched in order to find whether any derivative of this substance had been prepared which would, in the meantime, serve the object in view, and it was found that during their experiments on the formation of ethyl 1-cyano-*cyclo*propane-1-carboxylate (V) by the action of ethyl sodiocyanoacetate on ethylene dibromide, Carpenter and Perkin (Trans., 1899, **75**, 921) had isolated a substance melting at 119·5° which they considered to be ethyl αδ-dicyanovalerate (VI), because on alkaline hydrolysis it yielded adipic acid.

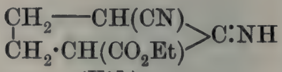


(V.)



$$\begin{array}{l} CH_2\cdot CH_2\cdot CN \\ | \\ CH_2\cdot CH(CO_2Et)\cdot CN \end{array}$$

(VI.)



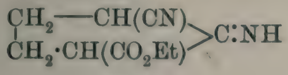
(VII.)

It was at once apparent that this substance would serve our purpose just as well as αδ-dicyanobutane, for, as it contains a primary nitrile group, it should yield ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) on treatment with sodium ethoxide.

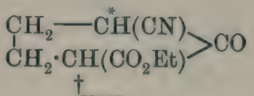
Carpenter and Perkin stated that they wished to reserve the further study of the substances described by them in their paper, but shortly after its publication Professor Carpenter left the University of Manchester and, in consequence, further work was abandoned. We have with their consent undertaken a complete study of this by-product prepared by them.

The substance described as ethyl αδ-dicyanovalerate (VI) is isolated from the products of the condensation of ethyl sodiocyanoacetate with ethylene dibromide after ethyl 1-cyano*cyclo*propane-1-carboxylate (V) and unchanged reacting substances have been separated by distillation with steam. It is purified by washing with cold alcohol, in which it is sparingly soluble, and is converted, as the authors found, almost quantitatively into adipic acid on hydrolysis, first with aqueous potassium hydroxide and finally with dilute sulphuric acid. There are, however, certain peculiarities about this substance which led us, in the light of experience gained during our study of imino-compounds, to doubt the constitution assigned to it by Carpenter and Perkin.

In the first place the compound is formed in a solution which must contain some free sodium ethoxide, and consequently, if there is as great a tendency to form the five-carbon alicyclic ring as there is in the case of *o*-phenylenediacetonitrile, it ought to be ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) and not ethyl αδ-dicyanovalerate (VI). Moreover, the high melting point of the substance taken in conjunction with its insolubility in cold alcohol seemed to suggest an imino-compound rather than a nitrile-carboxylic ester. All doubts on this point were set at rest when the substance melting at 119·5° was treated with acid hydrolysing agents, for on shaking with concentrated hydrochloric acid it at once passed into solution, from which a precipitate of ammonium chloride separated on standing. When water was added to this solution, an oil separated which gave an intense violet coloration with ferric chloride and on examination proved to be ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII).

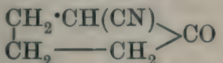


(VII.)

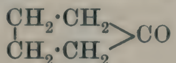


(VIII.)

Further proof in favour of this view of the constitution of the substance melting at 119·5° is afforded by its behaviour when distilled in a current of steam from dilute sulphuric acid, for under these conditions cyano*cyclo*pentan-1-one (IX) passes over with the steam. Moreover, if it is heated for some time with dilute sulphuric acid previous to distillation with steam, *cyclo*pentanone (X) passes over



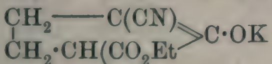
(IX.)



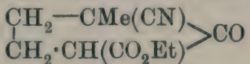
(X.)

and can be recovered from the distillate.

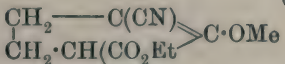
As already mentioned, ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) when treated with cold concentrated hydrochloric acid is completely transformed into ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII). This substance is a strong acid, dissolving in solutions of alkali carbonates with effervescence and giving in alcoholic solution an intense violet coloration with ferric chloride. It readily forms a crystalline monopotassium salt, which probably has the formula (XI), and on treatment in alcoholic solution with methyl iodide is converted almost completely into the *C*-methyl derivative, ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate (XII),



(XI.)

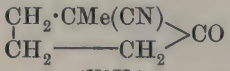


(XII.)



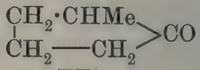
(XIII.)

although subsequent experiments on the hydrolysis of this substance showed that it contained a small quantity of the corresponding *O*-methyl derivative (XIII). It is of course evident that in the mono-alkylation of a substance of the constitution of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII) the alkyl group might unite either with the carbon atom marked (*) or that marked (†), both carbon atoms being attached to the carbonyl group and having in the one case a nitrile group and in the other a carbethoxyl group attached. The proof that the carbon atom attached to the nitrile group is the one first affected is given by the fact that ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate (XII) on distillation from dilute sulphuric acid in a current of steam yields 2-cyano-2-methyl*cyclo*pentan-1-one (XIV) identical with the compound prepared by the methylation of 2-cyano*cyclo*pentan-1-one (IX) by means of sodium ethoxide and methyl iodide.



$$\left.\begin{array}{l}CH_2\cdot CMe(CN)\\ CH_2\text{———}CH_2\end{array}\right>CO$$

(XIV.)

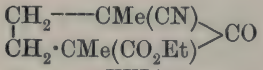


$$\left.\begin{array}{l}CH_2\cdot CHMe\\ CH_2\text{—}CH_2\end{array}\right>CO$$

(XV.)

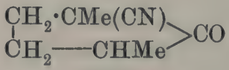
The prolonged action of sulphuric acid on 2-cyano-2-methyl*cyclo*pentan-1-one leads to the formation of 2-methyl*cyclo*pentan-1-one (XV).

The further methylation of ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate (XII) by means of sodium ethoxide and methyl iodide yields the dimethyl derivative, ethyl 5-cyano-2 : 5-dimethyl*cyclo*pentan-1-one-2-carboxylate (XVI), from which on distillation from dilute sulphuric acid 2-cyano-2 : 5-dimethyl*cyclo*pentan-1-one (XVII) can be obtained.



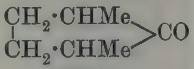
$$\left.\begin{array}{l}CH_2\text{——}CMe(CN)\\ CH_2\cdot CMe(CO_2Et)\end{array}\right>CO$$

(XVI.)



$$\left.\begin{array}{l}CH_2\cdot CMe(CN)\\ CH_2\text{——}CHMe\end{array}\right>CO$$

(XVII.)

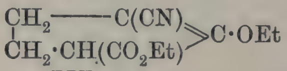


$$\left.\begin{array}{l}CH_2\cdot CHMe\\ CH_2\cdot CHMe\end{array}\right>CO$$

(XVIII.)

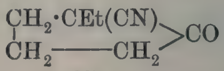
This substance on further treatment with sulphuric acid yields 2 : 5-dimethyl*cyclo*pentan-1-one (XVIII).

The ethylation of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII) through the pure potassium compound and ethyl iodide leads to the formation of a product which consists for the most part of the *O*-ethyl derivative (XIX), although a small quantity of the *C*-ethyl derivative (XX) is also formed at the same time.



$$\left.\begin{array}{l}CH_2\text{———}C(CN)\\ CH_2\cdot CH(CO_2Et)\end{array}\right>C\cdot OEt$$

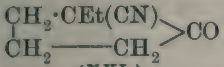
(XIX.)



$$\left.\begin{array}{l}CH_2\cdot CEt(CN)\\ CH_2\text{———}CH_2\end{array}\right>CO$$

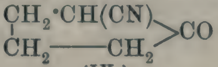
(XX.)

It was not found possible to separate this mixture, but from the following considerations it is evident that both these compounds were present in it. In the first place it is evident that when the potassium salt of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (XI), which is quite stable in aqueous solution, is acted on by an alcoholic solution of ethyl iodide, the product, obtained by adding water and extracting with ether, cannot contain any unchanged ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII). It gives, however, a red coloration with ferric chloride, and must therefore contain some of the *C*-ethyl derivative (XX). This conclusion was confirmed by a study of the products formed during the acid hydrolysis of the mixture, for on distilling it from dilute sulphuric acid in a current of steam, both 2-cyano-2-ethyl*cyclo*pentan-1-one (XXI) and 2-cyano*cyclo*pentan-1-one (IX) were obtained, the two compounds being readily separated by fractional distillation and



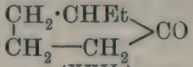
$$\begin{array}{l}CH_2\cdot CEt(CN)\\ CH_2 — CH_2\end{array}\!\!>CO$$

(XXI.)



$$\begin{array}{l}CH_2\cdot CH(CN)\\ CH_2 — CH_2\end{array}\!\!>CO$$

(IX.)



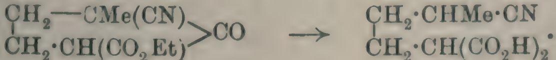
$$\begin{array}{l}CH_2\cdot CHEt\\ CH_2 — CH_2\end{array}\!\!>CO$$

(XXII.)

identified by means of their semicarbazones. The ethyl derivative (XXI) is identical with the compound prepared by the ethylation of 2-cyano*cyclo*pentan-1-one (IX) by means of sodium ethoxide and ethyl iodide, and its formation furnishes therefore another proof of the greater reactivity of the hydrogen atom combined with the carbon atom attached to the nitrile group of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII). 2-Cyano-2-ethyl*cyclo*pentan-1-one (XXI) is transformed by the further action of sulphuric acid into 2-ethyl*cyclo*pentan-1-one (XXII).

The proportion of the two constituents present in the product formed by the ethylation of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate was determined by careful alkaline hydrolysis, for whereas under these conditions, the *C*-ethyl derivative is broken down into aliphatic degradation products, the *O*-ethyl derivative is hydrolysed to ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII), which, presumably on account of the formation of its alkali salt, is stable towards dilute alkalis and can be recovered on acidifying the alkaline solution. The proportion was found to be almost four parts of the *O*-ethyl derivative to one part of the *C*-ethyl derivative.

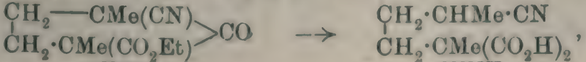
The derivatives of *cyclo*pentanone described in this communication are, as already indicated, exceedingly stable towards acid hydrolysing agents, and in no case investigated did the use of these reagents lead to the fission of the five-carbon ring, but, so long as the nitrile or carbethoxyl group remains attached to the carbon atom adjacent to the carbonyl group, they are, with the exception of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (VIII), at once acted on by dilute alkalis, passing with fission of the *cyclo*pentane ring into derivatives of adipic acid; thus ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate (XII) when warmed with alcoholic potash yields a potassium salt, from which δ-cyanobutylmalonic acid (XXIII) can be obtained on acidifying:



$$\begin{array}{l}CH_2 — CMe(CN)\\ CH_2\cdot CH(CO_2Et)\end{array}\!\!>CO \longrightarrow \begin{array}{l}CH_2\cdot CHMe\cdot CN\\ CH_2\cdot CH(CO_2H)_2\end{array}.$$

(XII.) (XXIII.)

In the same way ethyl 5-cyano-2:5-dimethyl*cyclo*pentan-1-one-2-carboxylate (XVI) yields δ-cyanomethylbutylmalonic acid (XXIV):

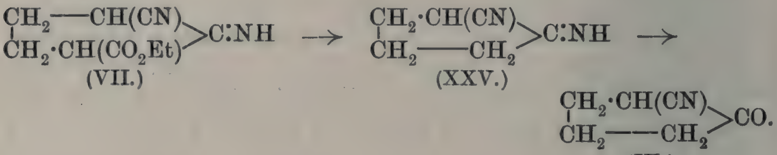


$$\begin{array}{l}CH_2 — CMe(CN)\\ CH_2\cdot CMe(CO_2Et)\end{array}\!\!>CO \longrightarrow \begin{array}{l}CH_2\cdot CHMe\cdot CN\\ CH_2\cdot CMe(CO_2H)_2\end{array},$$

(XVI.) (XXIV.

and on heating these dicarboxylic acids at 180°, δ-cyanohexoic acid, $CN\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, and δ-cyano-α-methylhexoic acid, $CN\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$, may be obtained. Finally, by the prolonged action of potassium hydroxide, the nitrile groups are hydrolysed and α-methyladipic and αα′-dimethyladipic acids are formed.

The imino-derivatives of *cyclo*pentane are, however, exceedingly stable towards alkaline hydrolysing agents, although, as mentioned above, when treated with acids they are at once converted into the corresponding ketones; thus ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) on warming with aqueous potassium hydroxide rapidly dissolves, and if the solution is cautiously acidified with acetic acid, carbon dioxide is eliminated and 1-imino-2-cyano*cyclo*pentane (XXV) is precipitated :

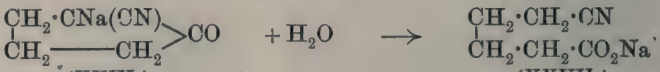


$$\left.\begin{array}{l}\mathrm{CH_2{-}\!{-}CH(CN)}\\ \mathrm{CH_2\cdot CH(CO_2Et)}\end{array}\right>\mathrm{C{:}NH} \longrightarrow \left.\begin{array}{l}\mathrm{CH_2\cdot CH(CN)}\\ \mathrm{CH_2{-}\!{-}CH_2}\end{array}\right>\mathrm{C{:}NH} \longrightarrow \left.\begin{array}{l}\mathrm{CH_2\cdot CH(CN)}\\ \mathrm{CH_2{-}\!{-}CH_2}\end{array}\right>\mathrm{CO}.$$

(VII.) (XXV.) (IX.)

This imino-compound is at once acted on by dilute hydrochloric acid, forming 2-cyano*cyclo*pentan-1-one (IX), a compound which resembles ethyl cyanoacetate in many of its properties; thus when treated with an equivalent of alcoholic sodium ethoxide it yields a sodium derivative (XXVI) insoluble in cold alcohol, which on treatment with methyl iodide yields 2-cyano-2-methyl*cyclo*pentan-1-one (XIV), and with ethyl iodide is converted into 2-cyano-2-ethyl*cyclo*pentan-1-one (XXI), the formation of these substances affording the proof required for establishing the constitution of the *C*-alkyl derivatives of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate.

This sodium compound is a remarkable example of the sensitiveness of the *cyclo*pentane ring in this condition towards alkalis, for it at once dissociates on being dissolved in water, forming the sodium salt of δ-cyanovaleric acid (XXVII):

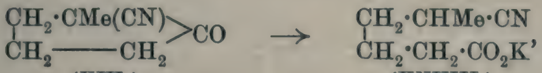


$$\left.\begin{array}{l}\mathrm{CH_2\cdot CNa(CN)}\\ \mathrm{CH_2{-}\!{-}CH_2}\end{array}\right>\mathrm{CO} \quad + \mathrm{H_2O} \longrightarrow \begin{array}{l}\mathrm{CH_2\cdot CH_2\cdot CN}\\ \mathrm{CH_2\cdot CH_2\cdot CO_2Na}\end{array}$$

(XXVI.) (XXVII.)

δ-Cyanovaleric acid has been prepared by Dieckmann (*Ber.*, 1900, **33**, 579), and is described as an oil. We have not succeeded in preparing either this substance or any of its homologues in a crystalline condition.

The same property is shown by the alkyl derivatives of 2-cyano-*cyclo*pentan-1-one, for when 2-cyano-2-methyl*cyclo*pentan-1-one (XIV) is warmed with aqueous potassium hydroxide it passes at once into the potassium salt of δ-cyanohexoic acid (XXVIII):



$$\begin{matrix} CH_2\cdot CMe(CN) \\ | \\ CH_2 \text{——} CH_2 \end{matrix} > CO \longrightarrow \begin{matrix} CH_2\cdot CHMe\cdot CN \\ | \\ CH_2\cdot CH_2\cdot CO_2K \end{matrix}$$

(XIV.) (XXVIII.)

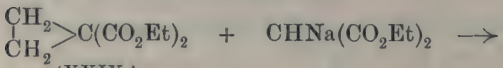
and in the same manner 2-cyano-2-ethyl*cyclo*pentan-1-one (XXI) passes into δ-cyanoheptoic acid, $CHEt(CN)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.

2-Cyano*cyclo*pentan-1-one and its alkyl derivatives are readily converted on treatment with sulphuric acid and distillation in a current of steam into the corresponding derivatives of *cyclo*pentanone.

The ketones described in this communication were characterised by the formation of semicarbazones, and in cases where this formation did not take place, by the formation of anilides. 2-Methyl*cyclo*pentan-1-one has been prepared by Bouveault (*Bull. Soc. chim.*, 1899, [iii], **21**, 1022) and by Wallach (*Annalen*, 1904, **331**, 319), who prepared its semicarbazone. 2 : 5-Dimethyl*cyclo*pentan-1-one has been prepared by Zelinsky and Rudsky (*Ber.*, 1896, **29**, 404), but these chemists do not seem to have characterised the ketone by the formation of a crystalline derivative.

As already mentioned, ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) occurs as a by-product in the formation of ethyl 1-cyano*cyclo*propane-1-carboxylate by the condensation of ethylene dibromide with the sodium compound of ethyl cyanoacetate, but the amount formed is not large, and we therefore had to seek some other method for the preparation of this substance in quantity. Although, initially, we used the method recommended by Carpenter and Perkin (*loc. cit.*), in which the mixture is heated in soda-water bottles at 100°, yet we found that the many disadvantages attaching to the use of soda-water bottles were not compensated by a very largely increased yield of the imino-compound; moreover, since it was subsequently found that the ethyl 1-cyano*cyclo*propane-1-carboxylate formed in the reaction could be readily converted into ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate, the condensation was always effected in Geissler flasks at the temperature of the water-bath. Ultimately, it was discovered that ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate could be prepared from ethyl 1-cyano*cyclo*propane-1-carboxylate by the following reaction.

Bone and Perkin (Trans., 1895, **67**, 108) have shown that when ethyl *cyclo*propane-1 : 1-dicarboxylate (XXIX) is treated with ethyl sodiomalonate, the *cyclo*propane ring is broken between the carbon atoms 1 and 2, condensation ensues, and ethyl butane-ααδδ-tetracarboxylate (XXX) is formed, thus:



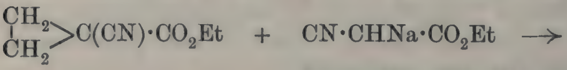
$$\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\!\!>C(CO_2Et)_2 \quad + \quad CHNa(CO_2Et)_2 \longrightarrow$$

(XXIX.)

$$(CO_2Et)_2CNa\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2.$$

(XXX.)

This remarkable reaction at once indicated a method by which ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate could be prepared, since by substituting ethyl sodiocyanoacetate and ethyl 1-cyano*cyclo*propane-1-carboxylate for the compounds used by Bone and Perkin, ethyl αδ-dicyanoadipate (XXXI) should be formed, thus:



$$\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\!\!>C(CN)\cdot CO_2Et \quad + \quad CN\cdot CHNa\cdot CO_2Et \longrightarrow$$

$$CO_2Et\cdot CNa(CN)\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et.$$

(XXXI.)

Ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate should then be readily formed from the above condensation product by the action of sodium ethoxide, if, indeed, it was not formed directly in the condensation in the same manner as in the interaction of ethyl sodiocyanoacetate and ethylene dibromide.

It was found that ethyl sodiocyanoacetate reacted vigorously with ethyl 1-cyano*cyclo*propane-1-carboxylate, and that under the experimental conditions described later, a satisfactory yield of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate was obtained; moreover, on examining the low boiling products from the condensation, a considerable quantity of ethyl carbonate was isolated.

The formation of ethyl carbonate in this reaction throws some light, not only on the mechanism of the condensation in the present instance, but also in a number of similar cases in which the loss of a carbethoxyl group has been noticed in condensations of this character; thus Moore (Trans., 1904, **85**, 165) showed that the substance obtained by Baeyer (*Ber.*, 1885, **18**, 3457) by the interaction of ethyl malonate and its sodium derivative, and described as ethyl phloroglucinoltricarboxylate, is in reality ethyl phloroglucinoldicarboxylate, and that a carbethoxyl group had been eliminated during the condensation. Although presumably unacquainted with this fact, Willstätter (*Ber.*, 1899, **32**, 1272), after he had detected ethyl acetate as one of the products of the condensation, suggested that ethyl carbonate was probably formed thus:

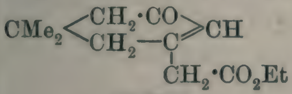
$$CH_2(CO_2Et)_2 + EtOH \longrightarrow CH_3\cdot CO_2Et + CO(OEt)_2,$$

and although he was unable to isolate this substance, yet Leuchs and Geserick (*Ber.*, 1908, **41**, 4371) have quite recently succeeded in doing so. It is probable, however, that the ethyl carbonate is formed in the reaction by the action of sodium ethoxide after the closing of the ring, since it has been shown that under certain conditions the elimination of a carbethoxyl group takes place readily in this manner; thus Thorpe (Trans., 1905, **87**, 1681) and Rogerson and Thorpe (*ibid.*, 1702) have shown that when ethyl α-cyano-*αβγ*-trimethylglutaconate (XXXII) is treated with sodium ethoxide in the presence of alcohol, it is quantitatively converted into ethyl carbonate and ethyl γ-cyano-*αβγ*-trimethylcrotonate (XXXIII):

$$\underset{\text{(XXXII.)}}{\mathrm{CO_2Et{\cdot}CMe{:}CMe{\cdot}CMe(CN){\cdot}CO_2Et}} + \mathrm{EtOH} \longrightarrow$$

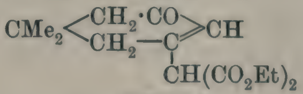
$$\underset{\text{(XXXIII.)}}{\mathrm{CO_2Et{\cdot}CHMe{\cdot}CMe{:}CMe{\cdot}CN}} + \mathrm{CO(OEt)_2}.$$

Another instance of the same kind is mentioned by Crossley and Gilling (Trans., 1909, **95**, 20), who found that when chlorodimethyl*cyclo*hexanone is condensed with ethyl sodiomalonate, the product is ethyl 1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one-5-acetate (XXXIV), instead of the ethyl salt of the dicarboxylic acid (XXXV), and that ethyl carbonate is one of the products (Proc., 1909, **25**, 96):



$$\mathrm{CMe_2}\!<\!{\mathrm{CH_2{\cdot}CO} \atop \mathrm{CH_2{-}\underset{\large\mathrm{CH_2{\cdot}CO_2Et}}{\overset{|}{C}}}}\!\!>\!\mathrm{CH}$$

(XXXIV.)

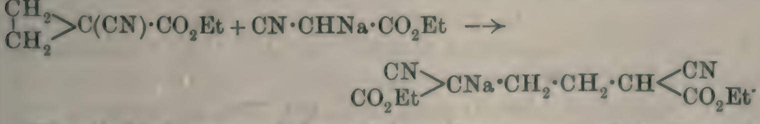


$$\mathrm{CMe_2}\!<\!{\mathrm{CH_2{\cdot}CO} \atop \mathrm{CH_2{-}\underset{\large\mathrm{CH(CO_2Et)_2}}{\overset{|}{C}}}}\!\!>\!\mathrm{CH}$$

(XXXV.)

Although it is probable that in some of the cases, in which the elimination of a carbethoxyl group has been effected in condensations involving the use of sodium ethoxide or an alkaline sodium derivative, such action may be due to hydrolysis and subsequent elimination of carbon dioxide, yet when this action is accompanied by the formation of ethyl carbonate, its cause is most probably due to spatial considerations, or, in other words, that the space formula of the substance does not admit of a carbethoxyl group being united with the carbon atom from which it is eliminated.

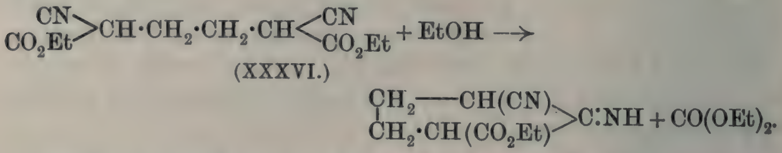
The proof that the carbethoxyl group is removed from ethyl *αδ*-dicyanoadipate (XXXVI) at the moment of its transformation into the *cyclo*pentane ring was supplied by preparing this ethyl salt and studying its behaviour towards sodium ethoxide. It may be prepared by condensing pure ethyl sodiocyanoacetate, carefully freed from alcohol, with ethyl 1-cyano*cyclo*propane-1-carboxylate in dry benzene, thus:



$$\left.{\mathrm{CH_2} \atop \mathrm{CH_2}}\right>\mathrm{C(CN){\cdot}CO_2Et} + \mathrm{CN{\cdot}CHNa{\cdot}CO_2Et} \longrightarrow$$

$$\left.{\mathrm{CN} \atop \mathrm{CO_2Et}}\right>\mathrm{CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CH}\left<{\mathrm{CN} \atop \mathrm{CO_2Et}}\right.{\cdot}$$

The ethyl salt prepared from this sodium compound by the action of water is a crystalline substance, which is quite stable, and when treated with an alcoholic solution of ethyl sodiocyanoacetate, passes into ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate and ethyl carbonate, thus:

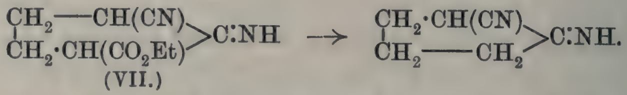


$$\begin{matrix}\mathrm{CN}\\ \mathrm{CO_2Et}\end{matrix}\!>\!\mathrm{CH\cdot CH_2\cdot CH_2\cdot CH}\!<\!\begin{matrix}\mathrm{CN}\\ \mathrm{CO_2Et}\end{matrix} + \mathrm{EtOH} \longrightarrow \begin{matrix}\mathrm{CH_2—CH(CN)}\\ \mathrm{CH_2\cdot CH(CO_2Et)}\end{matrix}\!>\!\mathrm{C{:}NH} + \mathrm{CO(OEt)_2}.$$

(XXXVI.)

It will be noticed that in closing the ring it was found convenient to use a small quantity of an alcoholic solution of ethyl sodiocyanoacetate rather than sodium ethoxide, and that the reaction is expressed in the equation as taking place through the agency of alcohol. This course was adopted after the behaviour of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate towards alcoholic sodium ethoxide had been studied.

It has been shown by one of us (Trans., 1904, **85**, 1728) that the hydrogen atom (*) of the complex $\cdot\mathrm{C({:}NH)\cdot}\overset{*}{\mathrm{C}}\mathrm{H(CN)\cdot CO_2Et}$ is replaceable by sodium on treatment with sodium ethoxide, whereas the hydrogen atoms of a complex $\cdot\mathrm{C({:}NH)\cdot CH_2\cdot CN}$ are not replaceable under these conditions (Trans., 1908, **93**, 170). In order to gain further evidence on this point we therefore treated ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate (VII) with sufficient sodium ethoxide and methyl iodide to replace two of the hydrogen atoms by methyl groups. The product was found to be, however, 1-imino-2-cyano*cyclo*pentane (XXV) mixed with other substances of higher molecular weight, and no trace of an alkyl derivative could be detected:



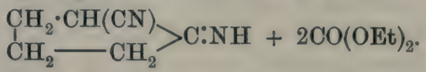
$$\begin{matrix}\mathrm{CH_2—CH(CN)}\\ \mathrm{CH_2\cdot CH(CO_2Et)}\end{matrix}\!>\!\mathrm{C{:}NH} \longrightarrow \begin{matrix}\mathrm{CH_2\cdot CH(CN)}\\ \mathrm{CH_2—CH_2}\end{matrix}\!>\!\mathrm{C{:}NH}.$$

(VII.)

It was evident therefore that sodium ethoxide had reacted on the imino-ester, causing the elimination of the carbethoxyl group, a conclusion which was confirmed by an experiment in which the action of sodium ethoxide alone was tried. Under these conditions, ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate is completely transformed into several products, from which considerable quantities of 1-imino-2-cyano*cyclo*pentane can be isolated. The other compounds formed, which are of higher molecular weight, have not yet been identified.

From these experiments it therefore follows that the hydrogen atoms of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate, like those of 2-imino-1-cyanohydrindene (Trans., 1908, **93**, 170), do not react with sodium ethoxide. It is evident, moreover, that if the transformation of ethyl αδ-dicyanoadipate into the alicyclic ring is effected by the action of sodium ethoxide, the product will be 1-imino-2-cyano*cyclo*pentane mixed with other substances, and not the imino-ester, thus :

$$CO_2Et\cdot CH(CN)\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et + 2EtOH \longrightarrow$$



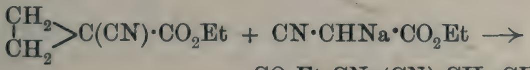
$$\left.\begin{array}{l}CH_2\cdot CH(CN)\\ |\\ CH_2 \text{———} CH_2\end{array}\right\rangle C{:}NH + 2CO(OEt)_2.$$

This conclusion was shown to be correct by actual experiment, although, as mentioned later, 1-imino-2-cyano*cyclo*pentane formed under these conditions is difficult to isolate, and it is more convenient to prepare this substance by another method.

Ultimately, it was found that a small quantity of alcoholic ethyl sodiocyanoacetate is sufficient to bring about the complete conversion of ethyl $\alpha\delta$-dicyanoadipate to ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate, and that the second carbethoxyl is not eliminated under these conditions. This discovery at once suggested a means by which a good yield of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate might be obtained by the condensation of ethyl 1-cyano*cyclo*propane-1-carboxylate with ethyl sodiocyanoacetate.

If molecular proportions of these ethyl esters are condensed in alcoholic solution, a yield of about 30 per cent. of the imino-ester is obtained if the reaction is stopped at an early stage, although this yield is considerably diminished if the action is allowed to continue. The reaction evidently proceeds in accordance with the equations :

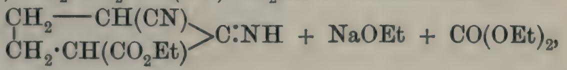
(1)



$$\left.\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\right\rangle C(CN)\cdot CO_2Et + CN\cdot CHNa\cdot CO_2Et \longrightarrow$$

$$CO_2Et\cdot CNa(CN)\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et.$$

(2) $CO_2Et\cdot CNa(CN)\cdot CH_2\cdot CH_2\cdot CH(CN)\cdot CO_2Et + 2HOEt \longrightarrow$



$$\left.\begin{array}{l}CH_2 \text{——} CH(CN)\\ |\\ CH_2\cdot CH(CO_2Et)\end{array}\right\rangle C{:}NH + NaOEt + CO(OEt)_2,$$

and the sodium ethoxide formed then reacts with the imino-ester, converting it gradually into 1-imino-2-cyano*cyclo*pentane and the other products mentioned above, which are always found accompanying the chief product of the condensation. It is apparent, therefore, that the difficulty can be overcome by using a sufficient excess of ethyl cyanoacetate to combine with the sodium ethoxide liberated during the reaction, or, in other words, a small quantity of ethyl sodiocyanoacetate dissolved in alcohol ought to be sufficient to convert any quantity of an equimolecular mixture of ethyl 1-cyano*cyclo*propane-1-carboxylate and ethyl cyanoacetate into ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate. This assumption was found to be correct, and a yield of 75 per cent. of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate was obtained on heating an equimolecular mixture of ethyl cyanoacetate and ethyl 1-cyano*cyclo*propane-1-carboxylate dissolved in alcohol containing a small quantity of ethyl sodiocyanoacetate.

It is of interest to note that the imino-derivatives of *cyclo*pentane described in this paper are all true imino-compounds, readily hydrolysed by dilute mineral acid to the corresponding ketones. In no case investigated did the compounds appear to react in the amino-form.

EXPERIMENTAL.

Formation of Ethyl 2-*Imino*-3-*cyano*cyclo*pentane*-1-*carboxylate* (VII, p. 686).

(1) *From Ethyl Sodiocyanoacetate and Ethylene Dibromide.*—The conditions used in this condensation were essentially the same as those recommended by Carpenter and Perkin, although it was found better to heat the mixture for three hours on the water-bath instead of working up the product immediately after the first reaction had subsided. After the reaction was finished, water was added, and the solution saturated with ammonium sulphate. The alcoholic solution, carrying all the organic products, rose to the top; it was separated, the alcohol evaporated off, and finally distilled in a current of steam. The non-volatile residue solidified on cooling, and was found to be nearly pure ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate. One crystallisation from benzene (it can also be crystallised from water or alcohol) rendered it pure, with a melting point of 119·5°, the same as that found by Carpenter and Perkin. It boiled without decomposition at 180°/15 mm.:

0·2333 gave 0·5148 CO_2 and 0·1434 H_2O. C = 60·16; H = 6·83.

$C_9H_{12}O_2N_2$ requires C = 60·0; H = 6·7 per cent.

The alcoholic washings from the purification of this substance on being diluted with water deposited a quantity of oil. After extraction by means of ether, the oil, on distillation, yielded two fractions: (*a*) 180—185°/15 mm., and (*b*) 200—210°/15 mm. Both fractions solidified on cooling; the former proved to be ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate, and the latter contained a substance much more soluble in alcohol than the imino-nitrile, which separated from dilute alcohol in small needles melting at 104°. The following analysis proved this substance to be *ethyl αδ-dicyanoadipate*,

$CO_2Et{\cdot}CH(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2Et$:

0·1819 gave 0·3826 CO_2 and 0·1028 H_2O. C = 57·36; H = 6·28.

$C_{12}H_{16}O_4N_2$ requires C = 57·2; H = 6·3 per cent.

Since this substance occurs later as the chief product in another reaction, its properties will be then described.

The steam distillate obtained in the original condensation contained some unchanged ethylene dibromide mixed with ethyl carbonate and ethyl 1-cyano*cyclo*propane-1-carboxylate. These compounds were separated in the first instance by slow distillation in a current of steam, when ethylene dibromide and ethyl carbonate passed over first and ethyl 1-cyano*cyclo*propane-1-carboxylate subsequently.

The point of separation was roughly gauged by noticing the moment at which the oil passing over ceased to sink at once in the condensed steam, and when this point was reached the receiver was changed and the nitrile ester collected. Complete separation was finally effected by extracting the steam distillates with ether and fractionally distilling the residues, after evaporating the ether. Ethyl 1-cyano*cyclo*propane-1-carboxylate, boiling at 210°/763 mm., was thus easily obtained pure, although the complete separation of ethyl carbonate and ethylene dibromide could not be entirely effected. By using a column, however, a fraction was obtained boiling at 126°, which contained only traces of bromine, and gave the following figures on analysis:

0·1881 gave 0·3475 CO_2 and 0·1375 H_2O. C = 50·39; H = 8·12.
$C_5H_{10}O_3$ requires C = 50·8; H = 8·5 per cent.

Although, owing to the presence of some ethylene dibromide, these figures do not agree very well with those required for ethyl carbonate, yet there can be no doubt that it consisted almost entirely of this ester. Since, however, this substance was clearly shown to be one of the products in the condensation of ethyl sodiocyanoacetate and ethyl 1-cyano*cyclo*propane-1-carboxylate (see p. 698), it was not thought necessary to attempt to purify it further in the present instance.

(2) *From Ethyl Sodiocyanoacetate and Ethyl* 1-*Cyano*cyclo*propane*-1-*carboxylate.*—When equimolecular quantities of these substances are dissolved in alcohol and heated on the water-bath, the insoluble sodium compound of the cyano-ester rapidly dissolves, and if the reaction is stopped at this stage and the products isolated in the same manner as described in the previous condensation, a yield of about 30 per cent. of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate is obtained together with some 1-imino-2-cyano*cyclo*pentane. As mentioned in the introduction, there are, however, other products formed in this reaction which are evidently of higher molecular weight, and although the constitutions of these have not as yet been ascertained, yet their formation is undoubtedly due to the presence of free sodium ethoxide generated in the course of reaction. In order to obviate this, an excess of ethyl cyanoacetate was used in the condensation, or, in other words, the condensation of the two ethyl salts was effected by means of a small quantity of ethyl sodiocyanoacetate. The conditions found most suitable were the following. Two grams of sodium were

dissolved in 50 grams of ethyl alcohol, and 10 grams of ethyl cyanoacetate added. Forty-eight grams of ethyl 1-cyano*cyclo*propane-1-carboxylate were then mixed with 39 grams of ethyl cyanoacetate, and the mixture added to the above solution, the whole being heated on the water-bath for four hours. At the end of this time a quantity of white solid had separated, which was collected, and proved to be the sodium compound of ethyl cyanoacetate.

The alcoholic filtrate from the above salt was mixed with water, yielding a neutral solution, which was distilled in a current of steam until free from volatile products. The oil remaining, which solidified on cooling, was collected, and the crude ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate obtained in this way purified by rubbing with cold alcohol and filtering, the solid being subsequently washed with cold alcohol until quite colourless. The product melted at 118—119°, and did not therefore require further recrystallising. The steam-distillate, on saturation with ammonium sulphate and extraction with ether,* yielded an oil practically the whole of which boiled between 120° and 130°, and, on redistillation, yielded pure ethyl carbonate boiling at 125°/763 mm.:

0·2062 gave 0·3843 CO_2 and 0·1541 H_2O. C = 50·81; H = 8·30.

$C_5H_{10}O_3$ requires C = 50·8; H = 8·5 per cent.

The identity of this substance was proved by the formation of carbamide on heating it with ammonia in a sealed tube at 180°. Only a very small quantity of ethyl 1-cyano*cyclo*propane-1-carboxylate was recovered unchanged, the yield of the imino-nitrile together with 1-imino-2-cyano*cyclo*pentane being about 75 per cent. of the theoretical amount. No ethyl *αδ*-*γ*-dicyanoadipate could be detected among the products of the reaction, for, although the alcoholic washings from the imino-nitrile precipitated an oil on the addition of water, yet, on standing, it again solidified, and was found to consist almost entirely of the imino-nitrile.

Ethyl αδ-Dicyanoadipate (XXXVI, p. 694) *and its Conversion into Ethyl* 2-*Imino*-3-*cyano*cyclo*pentane*-1-*carboxylate.*

The preparation of ethyl *αδ*-dicyanoadipate, unaccompanied by the imino-nitrile, was effected by condensing ethyl sodiocyanoacetate with ethyl 1-cyano*cyclo*propane-1-carboxylate under conditions in which no alcohol was present. Pure ethyl sodiocyanoacetate was prepared by dissolving 11·5 grams of sodium in 130 grams of alcohol, adding 57 grams of ethyl cyanoacetate, and mixing the solution with an equal volume of carefully dried ether. The white sodium compound was then collected and thoroughly washed with dry ether, for which purpose it was found more convenient to transfer the sodium compound to a flask and agitate with ether rather than to wash it on the filter funnel. The washing and filtering process was repeated four times, since it is essential to the success of the experiment that the last traces of alcohol should be removed. The sodium compound was finally dried on a porous plate and left in an evacuated desiccator over sulphuric acid for twenty-four hours. Twenty-seven grams of the dried sodium compound were suspended in 100 c.c. of carefully dried benzene and mixed with 28 grams of ethyl 1-cyano*cyclo*propane-1-carboxylate, the whole being heated on the water-bath for three hours. As the reaction proceeded, the white sodium compound became gradually yellow, and at the end of three hours the flask had become filled with a pale yellow, gelatinous solid. The product was then freed from benzene by distillation, dilute acetic acid added until faintly acid, and the whole distilled in a current of steam. Only a small quantity of oil, consisting for the most part of benzene, passed over, and the residue, which was a viscid oil, was isolated by means of ether, and on distillation under diminished pressure gave a principal fraction boiling at 208—210°/15 mm., which solidified on cooling. The solid was spread on a porous plate and crystallised from dilute alcohol, being obtained in small, colourless needles melting at 104°:

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* This method of treatment of the steam-distillate was used in each of the cases described later.

0·1811 gave 0·3792 CO_2 and 0·1031 H_2O. C = 57·11; H = 6·33.
$C_{12}H_{16}O_4N_2$ requires C = 57·2; H = 6·3 per cent.

Ethyl αδ-dicyanoadipate is very soluble in cold alcohol, and this property serves at once to distinguish it from ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate. No trace of this imino-nitrile could be detected among the low boiling products of this reaction.

Hydrolysis to Adipic Acid.—The constitution of the above ester was proved by its hydrolysis by means of alcoholic potash to adipic acid. Five grams were mixed with an alcoholic solution containing three times the calculated quantity of potash, and heated on the water-bath in a flask fitted with a reflux condenser for twelve hours. The alcohol was then evaporated, water added, and the solution boiled until ammonia ceased to be evolved, when the solution was acidified and yielded, on extraction with ether, a viscid oil which rapidly solidified. It crystallised from hot water in lustrous, colourless plates melting at 149°:

0·1750 gave 0·3160 CO_2 and 0·1091 H_2O. C = 49·25; H = 6·93.
$C_6H_{10}O_4$ requires C = 49·3; H = 6·9 per cent.

The acid is therefore evidently adipic acid.

*Conversion into Ethyl 2-Imino-3-cyano*cyclo*pentane-1-carboxylate.*—The transformation of ethyl αδ-dicyanoadipate into this imino-nitrile cannot be effected by the aid of sodium ethoxide, since this substance reacts further on the imino-nitrile, forming 1-imino-2-cyano*cyclo*pentane (see below), but a good yield may be obtained by employing the sodium compound of ethyl cyanoacetate in the following manner. Five grams of ethyl $\alpha\delta$-dicyanoadipate were dissolved in 20 c.c. of alcohol and the clear solution mixed with ethyl sodiocyanoacetate, prepared by adding 5 grams of ethyl cyanoacetate to a solution of 1 gram of sodium in alcohol. After warming on the water-bath for ten minutes, the solution was poured into water and distilled in a current of steam. The residue, which completely solidified on cooling, was collected, washed with cold alcohol until colourless, and crystallised from benzene, yielding the characteristic crystals of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate melting at 119°.

The steam distillate on extraction with ether was found to contain only ethyl carbonate boiling at 126°.

Conversion into 1-*Imino*-2-*cyano*cyclo*pentane.*—As mentioned above the action of alcoholic sodium ethoxide on ethyl $\alpha\delta$-dicyanoadipate leads to the formation of this imino-nitrile, but the conditions are difficult to regulate, and the description of the preparation and properties of the compound will therefore be reserved until later (p. 708). A considerable quantity may be obtained, however, in the following way. One gram of sodium is dissolved in 10 c.c. of alcohol and the solution added to 5 grams of the ethyl salt, also dissolved in alcohol. The solutions on being mixed become at once yellow and then rapidly darken, heat being generated at the same time. The reaction is finished at the end of three minutes, when an equal volume of water is added, and the clear solution rendered faintly acid by means of acetic acid. The solution is evaporated in a vacuum, when after some hours crystals separate which on recrystallisation from benzene yield long, flat needles melting at 147°. The identity of this substance with 1-imino-2-cyano*cyclo*pentane was established by direct comparison with the compound prepared by the method described on p. 708.

Ethyl 5-*Cyano*cyclo*pentan*-1-*one*-2-*carboxylate* (VIII, p. 687).

Twenty grams of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate were added to 100 grams of concentrated hydrochloric acid, and the clear yellow solution kept at the ordinary temperature for five minutes. An equal volume of water was then added, and the oil which separated was extracted with ether.

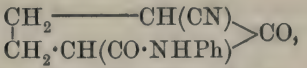
The keto-nitrile is appreciably soluble in dilute hydrochloric acid, and hence the above extraction with ether must be carried out at least four times. After washing the ethereal solution with water, the keto-nitrile was extracted from it with dilute sodium carbonate solution, which, on being acidified, deposited this substance as a heavy, colourless oil. By means of ether an oil was obtained which distilled at 172—174°/18 mm.:

0·1850 gave 0·4038 CO_2 and 0·1032 H_2O. C = 59·53 ; H = 6·19.

$C_9H_{11}O_3N$ requires C = 59·7 ; H = 6·1 per cent.

During the process of distillation, the keto-nitrile undergoes considerable decomposition, and much loss is entailed thereby. It is therefore advisable not to distil this substance, but to use the product obtained from the sodium carbonate extract, which is sufficiently pure for further work. The yield from the imino-nitrile is practically quantitative.

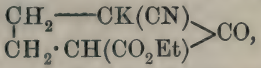
Ethyl 5-*cyanocyclopentan*-1-*one*-2-*carboxylate* is a fairly viscid, colourless oil, which dissolves in alkali carbonate solutions with effervescence. In alcoholic solution it gives a deep violet colour with ferric chloride.

2-*Cyano*-5-*carbanilinocyclopentan*-1-*one*,  $\begin{array}{l}CH_2\text{———}CH(CN)\\ CH_2\cdot CH(CO\cdot NHPh)\end{array}>CO$, is prepared by boiling the keto-nitrile with excess of aniline for five minutes and pouring the cooled solution into dilute hydrochloric acid. The oil, which remains undissolved, solidifies on keeping, and when crystallised from alcohol, yields white crystals resembling asbestos, which melt at 170°:

0·1801 gave 0·4534 CO_2 and 0·0920 H_2O. C = 68·65 ; H = 5·67.

0·2002 ,, 20·5 c.c. N_2 at 15° and 773 mm. N = 12·2.

$C_{13}H_{12}O_2N_2$ requires C = 68·4 ; H = 5·3 ; N = 12·3 per cent.

The *potassium* salt,  $\begin{array}{l}CH_2\text{——}CK(CN)\\ CH_2\cdot CH(CO_2Et)\end{array}>CO$, is precipitated in white crystals on adding an alcoholic solution containing the calculated quantity of potash to a solution of the ethyl salt in alcohol. It separates from hot methyl alcohol in needles, but is only sparingly soluble in hot ethyl alcohol:

0·1968 gave 0·0771 K_2SO_4. K = 17·56.

$C_9H_{10}O_3NK$ requires K = 17·8 per cent.

The potassium salt dissolves in water without change, and the solution, on acidifying, yields the ethyl salt from which the potassium salt was derived. The *silver* salt is prepared by adding the calculated quantity of silver nitrate solution to a solution of the potassium salt in water. When first precipitated, it is a white, curdy solid, which, however, rapidly becomes crystalline on shaking. It blackens on warming:

0·2345 gave 0·0876 Ag. Ag = 37·36.

$C_9H_{10}O_3NAg$ requires Ag = 37·5 per cent.

*The Products of Hydrolysis of Ethyl 5-Cyano*cyclo*pentan-1-one-2-carboxylate.*

(1) cyclo*Pentanone.*—This substance is the product of the complete acid hydrolysis of the above ester, and can be obtained in the following manner. Ten grams are added to 20 grams of concentrated sulphuric acid, and the solution kept at the ordinary temperature for three hours, when three times the volume of water is added and the solution heated under reflux for three hours. Distillation of the solution in a current of steam yields an oil which distils at 130°/756 mm. as a colourless, mobile liquid:

0·1921 gave 0·5015 CO_2 and 0·1660 H_2O. C = 71·21; H = 9·62.
C_5H_8O requires C = 71·4; H = 9·5 per cent.

The substance was characterised by the formation of the *semicarbazone*, which crystallises from alcohol in lustrous plates melting at 203°:

0·1893 gave 0·3535 CO_2 and 0·1349 H_2O. C = 50·92; H = 7·92.
$C_6H_{11}ON_3$ requires C = 51·1; H = 7·8 per cent.

(2) *2-Cyano*cyclo*pentan-1-one.*—The details of the preparation and the properties of this substance are given on p. 709.

(3) *Adipic Acid.*—Ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate, owing to the formation of the alkali salt, is very stable towards alkaline-hydrolysing agents, but on prolonged boiling ammonia is evolved, and if the action is continued until the evolution has ceased, the solution, on acidifying and extracting, yields adipic acid melting at 149°.

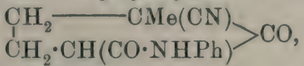
*Ethyl 5-Cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate* (XII, p. 687).

This substance is readily prepared by the action of methyl iodide on the potassium salt of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate, although subsequent experiments on its hydrolysis showed that a small quantity of the methoxy-derivative (XIII, p. 687) is formed at the same time. For this purpose 10 grams of the dried salt were suspended in absolute alcohol, mixed with excess of methyl iodide, and heated on the water-bath for three hours. The alcohol and excess of methyl iodide were then evaporated, water added, and the resulting oil, after extraction with ether, distilled without decomposition at 170—171°/18 mm.:

0·1873 gave 0·4209 CO_2 and 0·1151 H_2O. C = 61·29; H = 6·83.
$C_{10}H_{13}O_3N$ requires C = 61·5; H = 6·7 per cent.

The methyl derivative is insoluble in cold aqueous solutions of alkali carbonates and hydroxides. Its alcoholic solution gives an intense red coloration with ferric chloride.

*2-Cyano-5-carbanilino-2-methyl*cyclo*pentan-1-one,*



$$\begin{matrix} CH_2 - CMe(CN) \\ CH_2 \cdot CH(CO \cdot NHPh) \end{matrix} \!\!> CO,$$

is the only crystalline derivative we could prepare from the methyl derivative in order to characterise it. It is formed when the ethyl salt is boiled with excess of aniline for fifteen minutes, and is isolated by pouring the cooled product into dilute hydrochloric acid. The oil which remains undissolved slowly becomes solid, and when crystallised from ethyl alcohol, yields white, feathery needles melting at 163° :

0·2015 gave 0·5111 CO_2 and 0·1037 H_2O. C = 69·16 ; H = 5·71.

$C_{14}H_{14}O_2N_2$ requires C = 69·4 ; H = 5·8 per cent.

Ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate does not react with semicarbazide, and when treated with phenylhydrazine yields on oily phenylhydrazone which could not be crystallised.

*The Products of Hydrolysis of Ethyl 5-Cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate.*

(1) *2-Cyano-2-methyl*cyclo*pentan-1-one.*—A full description of the properties of this substance is given on p. 711, where another method for its preparation is described. Its formation from ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate in the present instance is of importance, however, as showing that the methyl group in the methylation of this ethyl salt attaches itself to the carbon atom united with the nitrile group and not to that attached to the carbethoxyl group.

The preparation can be effected as follows: Five grams of the ethyl salt are added to 100 c.c. of a 10 per cent. solution of sulphuric acid, and the mixture is slowly distilled in a current of steam. The keto-nitrile, as soon as formed, passes over, and is finally obtained as an oil distilling at 230°/765 mm. :

0·1795 gave 0·4451 CO_2 and 0·1165 H_2O. C = 67·92 ; H = 7·21.

C_7H_9ON requires C = 68·3 ; H = 7·3 per cent.

The compound was characterised as 5-cyano-5-methyl*cyclo*pentan-1-one by the formation of the semicarbazone melting at 210°.

(2) *2-Methyl*cyclo*pentan-1-one.*—This substance is the chief product of the prolonged action of dilute sulphuric acid on ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate, and can be isolated in the following way. Ten grams of the ethyl salt are mixed with 20 grams of concentrated sulphuric acid, and the clear solution kept at the ordinary temperature for six hours, when three times the volume of water is added, and

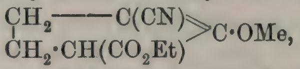
the solution boiled in a flask under reflux for three hours. The solution is then distilled in a current of steam, the distillate furnishing 2-methyl*cyclo*pentan-1-one, boiling at 140°/765 mm., as found by Bouveault (*loc. cit.*) and Wallach (*loc. cit.*):

0·2103 gave 0·5657 CO_2 and 0·1951 H_2O. C = 73·37; H = 10·31.
$C_6H_{10}O$ requires C = 73·5; H = 10·2 per cent.

The semicarbazone, $C_7H_{13}ON_3$, crystallises from alcohol in colourless plates melting at 174—176° (compare Wallach, *loc. cit.*):

0·1924 gave 0·3812 CO_2 and 0·1473 H_2O. C = 54·03; H = 8·51.
$C_7H_{13}ON_3$ requires C = 54·2; H = 8·4 per cent.

(3) δ-*Cyanobutylmalonic Acid* (XXIII, p. 689).—Although exceedingly stable towards acid hydrolysing agents, the *cyclo*pentane ring is readily broken by the action of alkalis, and when ethyl 2-cyano-2-methyl*cyclo*pentane is warmed with alcoholic potash, it is completely transformed into the above acid. The conditions employed were as follows: Eight grams of the ethyl salt were added to a solution containing two equivalents of potash dissolved in alcohol, when heat was generated, the solution became pale brown in colour, and a test portion added to water was found to precipitate no oil. Water was then added and the alcohol evaporated, the solution being subsequently acidified by means of hydrochloric acid. On adding the acid, a small quantity of oil separated, which was separated by means of ether and proved to be ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate. It is evident therefore that a small quantity of the methoxy-derivative,



$$\left.\begin{array}{l}CH_2\text{———}C(CN)\\ CH_2\cdot CH(CO_2Et)\end{array}\right> C\cdot OMe,$$

had been formed in the methylation of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate. The mother liquor was then saturated with ammonium sulphate and extracted with ether, by which means a thick syrup was obtained which gradually solidified. The solid was spread on a porous plate and crystallised from dilute hydrochloric acid, from which colourless needles separated, melting at 95°, and evolving carbon dioxide at 170°:

0·1872 gave 0·3550 CO_2 and 0·1005 H_2O. C = 51·71; H = 4·97.
$C_8H_{11}O_4N$ requires C = 51·9; H = 5·9 per cent.

The *silver* salt, $C_8H_9O_4NAg_2$, is obtained as a white, crystalline precipitate on adding the calculated quantity of a solution of silver nitrate to a neutral solution of the ammonium salt of the acid:

0·2417 gave 0·1306 Ag. Ag = 54·02.
$C_8H_9O_4NAg_2$ requires Ag = 54·14 per cent.

(4) δ-*Cyanohexoic Acid*, $CN\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, *and* α-*Methyladipic Acid*, $CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.—The prepara-

tion of δ-cyanohexoic acid is described on p. 712, and its properties are given there. It is formed in the present instance by heating δ-cyanobutylmalonic acid at 180° until the evolution of carbon dioxide has ceased. The oily product did not solidify. Methyladipic acid is formed by the prolonged action of aqueous potassium hydroxide on δ-cyanohexoic acid, the experimental conditions being also described on p. 712

Ethyl 5-*Cyano*-2 : 5-*dimethyl*cyclo*pentan*-1-*one*-2-*carboxylate* (XVI, p. 688).

The further methylation of ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate was effected by the aid of sodium ethoxide and methyl iodide in the following manner. Ten grams of the ethyl salt were added to an alcoholic solution containing 1·2 grams of sodium, and the solution after being mixed with 10 grams of methyl iodide was heated on the water-bath until neutral. The excess of methyl iodide was then distilled off, water added, and the oil extracted with ether. Since a test portion of the oil still gave a red colour with ferric chloride in alcoholic solution, the above operation was again repeated with the same quantities. The final ethereal extract yielded an oil which distilled at 182—183°/15 mm. as a colourless, fairly viscid liquid :

0·1947 gave 0·4489 CO_2 and 0·1280 H_2O. C = 62·87 ; H = 7·31.

$C_{11}H_{15}O_3N$ requires C = 63·1 ; H = 7·2 per cent.

The ethyl salt gave no coloration with ferric chloride.

The *semicarbazone*, $C_{12}H_{18}O_3N_4$, crystallises from alcohol in microscopic needles melting and decomposing at 193° :

0·1899 gave 0·3754 CO_2 and 0·1177 H_2O. C = 53·91 ; H = 6·89.

$C_{12}H_{18}O_3N_4$ requires C = 54·1 ; H = 6·8 per cent.

The Products of Hydrolysis of Ethyl 5-*Cyano*-2 : 5-*dimethyl*cyclo*pentan*-1-*one*-2-*carboxylate.*

(1) 2 : 5-*Dimethyl*cyclo*pentan*-1-*one.*—This substance is formed by the prolonged hydrolysis of ethyl 5-cyano-2 : 5-dimethyl*cyclo*pentan-1-one-2-carboxylate with sulphuric acid, and can be prepared in the following way. Five grams of the ethyl salt are mixed with 20 grams of concentrated sulphuric acid, and the clear solution is kept for six hours, when three times the volume of water is added and the solution boiled in a flask under reflux for three hours. On distillation in a current of steam, an oil is obtained which distils at 149°/758 mm. as a clear, mobile liquid :

0·2001 gave 0·5491 CO_2 and 0·1946 H_2O. C = 74·83 ; H = 10·81.

$C_7H_{12}O$ requires C = 75·0 ; H = 10·7 per cent.

Zelinsky and Rudsky (*Ber.*, 1895, **28**, 404) give 145—147° as the boiling point of this substance.

The *semicarbazone*, $C_8H_{15}ON_3$, crystallises from alcohol in colourless plates melting at 171°.

(2) 2-*Cyano*-2 : 5-*dimethyl*cyclo*pentan*-1-*one* (XVII, p. 688).—This substance was prepared by slowly distilling ethyl 5-cyano-2 : 5-dimethyl*cyclo*pentan-1-one-2-carboxylate (5 grams) from 10 per cent. sulphuric acid (100 c.c.) in a current of steam. The distillate furnished an oil, distilling at 241°/773 mm. as a colourless, mobile liquid :

0·1793 gave 0·4596 CO_2 and 0·1325 H_2O. C = 69·91 ; H = 8·21.

$C_8H_{11}ON$ requires C = 70·1 ; H = 8·0 per cent.

The keto-nitrile is sparingly soluble in cold water.

The *semicarbazone*, $C_9H_{14}ON_4$, separates from alcohol in colourless plates melting and decomposing at 205°.

(3) δ-*Cyanomethylbutylmalonic acid* (XXIV, p. 689) is formed by the hydrolysis of ethyl 5-cyano-2 : 5-dimethyl*cyclo*pentan-1-one-2-carboxylate by means of alcoholic potash in the following manner. Five grams of the ethyl salt were added to an alcoholic solution containing slightly more than the theoretical quantity of potash, and the solution heated on the water-bath until a test portion was completely soluble in water. Water was then added, the alcohol evaporated, the solution acidified, and extracted with ether. The ethereal solution yielded a thick syrup, which slowly set to a crystalline mass. It was purified by spreading on a porous plate and recrystallising from dilute hydrochloric acid, which gave microscopic needles melting at 106° and evolving carbon dioxide at 170° :

0·1915 gave 0·3835 CO_2 and 0·1093 H_2O. C = 54·61 ; H = 6·34.

$C_9H_{13}O_4N$ requires C = 54·3 ; H = 6·5 per cent.

The *silver* salt, $C_9H_{11}O_4NAg_2$, is a white, crystalline substance which rapidly darkens on warming :

0·2193 gave 0·1144 Ag. Ag = 52·17.

$C_9H_{11}O_4NAg$ requires Ag = 52·3.

(4) δ-*Cyano-α-methylhexoic Acid*, $CN\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$. —This substance can be prepared by heating δ-cyanomethylbutylmalonic acid under the following conditions. Three grams of the acid were heated in a test-tube placed in a bath of sulphuric acid until the evolution of carbon dioxide had ceased. The viscid liquid remaining, which did not solidify, was shaken with ether, and the ethereal solution after evaporation yielded a liquid which showed no signs of crystallising after being kept for several weeks in an evacuated desiccator :

0·1820 gave 0·4116 CO_2 and 0·1361 H_2O. C = 61·67 ; H = 8·31.

$C_8H_{13}O_2N$ requires C = 61·9 ; H = 8·4 per cent.

The *silver* salt, $C_8H_{12}O_2NAg$, separates from a neutral solution of the ammonium salt of the acid on addition of the calculated quantity of silver nitrate solution, as a white, gelatinous precipitate:

0·2181 gave 0·0895 Ag. Ag = 41·03.

$C_8H_{12}O_2NAg$ requires Ag = 41·2 per cent.

The salt is soluble in hot water, and separates from the solution on cooling in needles. The solution, however, rapidly darkens, unless cooled immediately.

(5) *αδ-Dimethyladipic Acid*, $CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H$.—The complete hydrolysis of ethyl 5-cyano-2:5-dimethyl*cyclo*pentan-1-one-2-carboxylate by means of alcoholic potash leads mainly to the formation of the α-modification of the above acid, although a small quantity of the β-modification was isolated from the mother liquors. The process adopted was as follows: Five grams of the ethyl salt were heated with a solution of one and a-half times the calculated quantity of potash dissolved in alcohol on the water-bath, water being added from time to time to replace the alcohol lost by evaporation. The process was continued for six hours, when the odour of ammonia ceased to be apparent. The solution was then acidified, saturated with ammonium sulphate, and extracted with ether. The ethereal solution yielded on evaporation a thick syrup which rapidly solidified. The solid was spread on a porous plate, and crystallised several times from water, ultimately yielding prisms melting at 140—141° (compare Zelinsky, *Ber.*, 1891, **24**, 4002):

0·1911 gave 0·3849 CO_2 and 0·1416 H_2O. C = 54·92; H = 8·23.

$C_8H_{14}O_4$ requires C = 55·1; H = 8·0 per cent.

The mother liquors on evaporation yielded a solid from which, by repeated recrystallisation, a small quantity of an acid melting at 74° was obtained. This was evidently the β-modification of the acid, but the quantity at our disposal was too small for further investigation.

Ethylation of Ethyl 5-*Cyano*cyclo*pentan*-1-*one*-2-*carboxylate.*

The ethylation of this ester was carried out in order to ascertain whether the ethyl group would attach itself to oxygen or to carbon, with the result that the product was found to consist of a mixture of about four parts of the *O*-ethyl derivative to one part of the *C*-ethyl derivative. The operation was effected in the same manner as in the corresponding methylation (p. 702). An oil was obtained which distilled at 190—191°/18 mm. as a fairly viscid, colourless liquid, the alcoholic solution of which gave a red colour with ferric chloride:

0·1987 gave 0·4575 CO_2 and 0·1303 H_2O. C = 62·80; H = 7·29.

$C_{11}H_{15}O_3N$ requires C = 63·1; H 7·2 per cent.

On account of the constant boiling point of this liquid, and the fact that it gave a coloration with ferric chloride, it was at first thought to be the pure *C*-ethyl derivative, but this view was at once found to be wrong when the behaviour of the substance towards alcoholic potash was studied; when it was warmed with an alcoholic solution containing two equivalents of potash, a clear solution was obtained on adding water, and on rendering the solution acid, ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate was precipitated. The quantity of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate regenerated in this manner showed that at least four-fifths of the above product of ethylation must have consisted of the *O*-ethyl derivative, and that the colour produced by ferric chloride must therefore have been due to the presence of a small quantity of the *C*-ethyl derivative. We were unable to devise any method for the separation of these two substances.

Acid Hydrolysis of the Mixture.—The presence of both the *C*-ethyl and *O*-ethyl derivatives of ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate in the product formed by the ethylation of the potassium salt of this substance was also demonstrated by distilling the mixture (20 grams) from 10 per cent. sulphuric acid (200 c.c.) in a current of steam, when both 2-cyano*cyclo*pentan-1-one and 2-cyano-2-ethyl*cyclo*pentane were formed. The distillate yielded an oil which on fractionation under ordinary pressure yielded ultimately two fractions: (*a*) 228—231°, giving a semicarbazone melting at 190°, and (*b*) 240—241°, giving a semicarbazone melting at 220°. The lower boiling fraction was therefore 2-cyano*cyclo*pentan-1-one and the higher boiling fraction was 2-cyano-2-ethyl*cyclo*pentan-1-one, the proportion of the two compounds being about four parts of the former to one part of the latter. This experiment therefore confirms the composition of this mixture ascertained by the alkaline hydrolysis in the manner stated above.

1-*Imino-2-cyano*cyclo*pentane* (IV, p. 685).

This substance was originally prepared in an attempt to methylate ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate by the action of sodium ethoxide and methyl iodide, and was found to be the sole product of this reaction. As it had evidently been formed by the elimination of the carbethoxyl group from this substance by the action of the sodium ethoxide, an attempt was made to prepare it by the action of this reagent alone, and a small yield was obtained by this means. The reaction is, however, difficult to control. Thus ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate, when added to an equivalent of sodium dissolved in alcohol, forms a pale yellow solution, which, however, rapidly darkens, and if, after the lapse of a few minutes, the solution is neutralised with acetic acid and the excess of alcohol evaporated in a vacuum, a residue remains which when treated with water yields a quantity of the above insoluble imino-nitrile. This substance can, however, be readily and quantitatively prepared from ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate by the following process. Ten grams of the ethyl salt are suspended in 20 c.c. of water and the mixture rendered strongly alkaline with aqueous potassium hydroxide. On warming to 50° and shaking, the ethyl salt quickly dissolves, and if the warm solution is at once acidified with acetic acid, carbon dioxide is at once evolved and 1-imino-2-cyano*cyclo*pentane separates out. The solution, however, must be only just acid, and it is better, in the first instance, to neutralise the solution with acetic acid and filter the imino-nitrile formed, subsequently adding more acetic acid to obtain a further quantity of this substance. This is advisable because excess of acetic acid slowly hydrolyses 1-imino-2-cyano*cyclo*pentane to 2-cyano*cyclo*pentan-1-one. 1-*Imino*-2-*cyano*cyclo*pentane* crystallises from benzene in long, flattened needles resembling *m*-dinitrobenzene in form and colour. It melts at 147° and distils at 271°/751 mm. without decomposition. At a lower temperature it sublimes in fern-like needles:

(1) 0·1880 gave 0·4609 CO_2 and 0·1269 H_2O. C = 66·86; H = 7·50.
(2) 0·1803 „ 0·4411 CO_2 „ 0·1260 H_2O. C = 66·72; H = 7·76.
$C_6H_8N_2$ requires C = 66·7; H = 7·4 per cent.

The imino-nitrile is sparingly soluble in cold ether and can be recrystallised from this solvent. It is sparingly soluble in cold alcohol, and can be recrystallised from hot water, but undergoes partial hydrolysis during the process. It dissolves instantly in dilute mineral acids, forming 2-cyano*cyclo*pentan-1-one and the ammonium salt of the acid used, but it is remarkably stable towards alkali hydroxides; thus it can be fused with concentrated aqueous potassium hydroxide at a temperature of 150°, and merely sublimes unchanged from the solution. We were in fact unable to prepare adipic acid from it by this method. The imino-nitrile reacts with phenylhydrazine in acetic acid solution, forming the phenylhydrazone of 2-cyano*cyclo*pentan-1-one, and with semicarbazide in acetic acid, forming the semicarbazone of this substance, but the formation of these compounds is evidently due to the hydrolysis of the imino-group by the acetic acid present. These substances are described below.

2-*Cyano*cyclo*pentan*-1-*one* (IX, p. 687).

This keto-nitrile can be prepared by the distillation of ethyl 2-imino-3-cyano*cyclo*pentane-1-carboxylate or ethyl 5-cyano*cyclo*pentan-1-one-2-carboxylate (10 grams) from their solutions in 10 per cent. sulphuric acid (100 c.c.) in a current of steam, and this is the best way of preparing this substance in quantity, since, owing to the fact that at the moment of its formation the keto-nitrile is removed by the steam, the formation of other products is prevented. It may also be prepared from 1-imino-2-cyano*cyclo*pentane by dissolving this imino-nitrile in dilute hydrochloric acid and, after saturating the solution with ammonium sulphate, extracting with ether. 2-*Cyano*cyclo*pentan*-1-*one* is a mobile oil which distils without decomposition at 229—230°/773 mm.:

0·1769 gave 0·4272 CO_2 and 0·0998 H_2O. C = 65·86; H = 6·26

C_6H_7ON requires C = 66·1; H = 6·4 per cent.

The keto-nitrile dissolves in about 20 volumes of cold water, and the solution gives a green colour with ferric chloride. It is insoluble in aqueous solutions of alkali hydroxides or carbonates, but is at once acted on by alcoholic potash or the warm aqueous alkali, forming δ-cyanovaleric acid (see below). It possesses a most characteristic odour.

The *semicarbazone*, $C_7H_{10}ON_4$, separates from alcohol, in which it is sparingly soluble, in small plates melting and decomposing at 190°:

0·1931 gave 0·3595 CO_2 and 0·1076 H_2O. C = 50·77; H = 6·19.

$C_7H_{10}ON_4$ requires C = 50·6; H = 6·0 per cent.

The *phenylhydrazone*, $C_{12}H_{13}N_3$, crystallises from alcohol in colourless needles melting at 126°:

0·1864 gave 0·4959 CO_2 and 0·1137 H_2O. C = 72·55; H = 6·77.

$C_{12}H_{13}N_3$ requires C = 72·4; H = 6·5 per cent.

The *sodium* compound, C_6H_6ONNa, separates as a crystalline precipitate on adding an alcoholic solution containing the calculated quantity of sodium ethoxide to an alcoholic solution of the keto-nitrile. It is sparingly soluble in hot alcohol, but separates from a large volume of this solvent in fine needles

0·2359 gave 0·1275 Na_2SO_4. Na = 17·51.

C_6H_6ONNa requires Na = 17·6 per cent.

The sodium compound readily dissolves in water with immediate dissociation, forming the sodium salt of δ-cyanovaleric acid.

The Products of Hydrolysis of 2-*Cyano*cyclo*pentan*-1-*one.*

(1) cyclo*Pentanone.*—The *cyclo*pentane ring is stable towards acid hydrolysing agents, and if 2-cyano*cyclo*pentan-1-one is boiled with dilute sulphuric acid for six hours and the product distilled in a current of steam, *cyclo*pentanone passes over.

It was characterised by the formation of its semicarbazone melting at 203°.

(2) δ-*Cyanovaleric Acid* (XXVII, p. 690).—This is at once formed

by the action of alkali hydroxides in alcoholic solution on 2-cyano*cyclo*pentan-1-one, but is best prepared by dissolving the sodium compound of this substance in water, acidifying the solution with hydrochloric acid, and extracting with ether. The acid appears to be a liquid at the ordinary temperature (compare Dieckmann, *Ber.*, 1900, **33**, 574):

0·1891 gave 0·3912 CO_2 and 0·1186 H_2O. C = 56·42; H = 6·97.
$C_6H_9O_2N$ requires C = 56·7; H = 7·1 per cent.

The *silver* salt, $C_6H_8O_2NAg$, is precipitated from a neutral solution of the ammonium salt of the acid on adding the calculated quantity of silver nitrate solution. It is a white, crystalline powder which darkens on exposure to light:

0·2179 gave 0·1004 Ag. Ag = 46·07.
$C_6H_8O_2NAg$ requires Ag = 46·2 per cent.

By the further action of aqueous potassium hydroxide on δ-cyanovaleric acid, ammonia is evolved, and if the action is continued until the evolution has ceased, the solution on acidifying with hydrochloric acid and extracting with ether yields adipic acid melting at 149°.

2-*Cyano-2-methyl*cyclo*pentan-1-one* (XIV, p. 688).

This compound can be readily prepared from 2-cyano*cyclo*pentan-1-one in the following way. Ten grams of the keto-nitrile are mixed with an equal volume of alcohol, and the solution added to an alcoholic solution of 2·2 grams of sodium. The sodium compound, which is very sparingly soluble in cold alcohol, separates quantitatively, and is collected and washed with alcohol. It is then suspended in alcohol, mixed with excess of methyl iodide, and heated on the water-bath under a reflux condenser for three hours, when the sodium compound will have dissolved. The alcohol and excess of methyl iodide are then evaporated, and after extraction with ether an oil is obtained which distils at 230°/764 mm. as a clear, mobile liquid:

0·1795 gave 0·4451 CO_2 and 0·1165 H_2O. C = 67·92; H = 7·21.
C_7H_9ON requires C = 68·3; H = 7·3 per cent.

The keto-nitrile is soluble in about 30 volumes of water, and gives no colour with ferric chloride. It is insoluble in cold alkali hydroxides, but is immediately hydrolysed on warming, yielding δ-cyanohexoic acid.

The *semicarbazone*, $C_8H_{12}ON_4$, crystallises from alcohol in glistening plates melting and decomposing at 210°:

0·1860 gave 0·3609 CO_2 and 0·1041 H_2O. C = 52·91; H = 6·22.
$C_8H_{12}ON$ requires C = 53·3; H = 6·7 per cent.

The Products of Hydrolysis of 2-*Cyano*-2-*methyl*cyclo*pentan*-1-*one.*

(1) 2-*Methyl*cyclo*pentan*-1-*one.*—This substance is formed when 2-cyano-2-methyl*cyclo*pentan-1-one is boiled for six hours with dilute sulphuric acid, and is isolated by distilling the product in a current of steam. The details of the method are given on page 703, where the formation of this substance from ethyl 5-cyano-5-methyl*cyclo*pentan-1-one-2-carboxylate is described.

(2) δ-*Cyanohexoic Acid*, $CN\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.—This is best prepared by the action of alcoholic potash on the keto-nitrile. Five grams are added to an alcoholic solution of the calculated quantity of potash, when much heat is generated, and the solution becomes first dark brown and then pale yellow. The alcohol is evaporated, water added, the solution acidified with hydrochloric acid, and extracted with ether. The ethereal extract yields the acid as a viscid oil which could not be crystallised :

0·1903 gave 0·4130 CO_2 and 0·1320 H_2O. C = 59·19 ; H = 7·71.

$C_7H_{11}O_2N$ requires C = 59·6 ; H = 7·8 per cent.

The *silver* salt, $C_7H_{10}O_2NAg$, is precipitated as a white, microcrystalline solid on adding the calculated quantity of silver nitrate solution to a neutral solution of the ammonium salt of the acid. It darkens on exposure to light :

0·2213 gave 0·0961 Ag. Ag = 43·42.

$C_7H_{10}O_2NAg$ requires Ag = 43·5 per cent.

The further action of excess of aqueous potassium hydroxide on δ-cyanohexoic acid causes ammonia to be evolved, and if the solution is heated until the evolution has ceased and then acidified and extracted with ether, α-methyladipic acid,

$$CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

melting at 64°, is obtained (compare Bone and Perkin, Trans., 1895, **67**, 115 ; Montemartini, *Gazzetta*, 1896, **26**, ii, 278) :

0·2012 gave 0·3866 CO_2 and 0·1380 H_2O. C = 52·41 ; H = 7·62.

$C_7H_{12}O_4$ requires C = 52·5 ; H = 7·5 per cent.

2-*Cyano*-2-*ethyl*cyclo*pentan*-1-*one* (XX, p. 688).

The conditions for the preparation of this ethyl derivative are the same as those just described for the methyl derivative. It is a mobile oil, which distils at 241°/769 mm. as a colourless liquid :

0·1896 gave 0·4868 CO_2 and 0·1401 H_2O. C = 70·01 ; H = 8·21.

$C_8H_{11}ON$ requires C = 70·1 ; H = 8·0 per cent.

The keto-nitrile is sparingly soluble in cold water, and is insoluble in cold potassium hydroxide solution. It is, however, immediately hydrolysed on warming, forming the potassium salt of δ-cyanoheptoic acid.

The *semicarbazone*, $C_9H_{14}ON_4$, separates from alcohol in colourless plates melting at 220°:

0·2107 gave 0·4293 CO_2 and 0·1396 H_2O. C = 55·57; H = 7·36.
$C_9H_{14}ON_4$ requires C = 55·7; H = 7·2 per cent.

The Products of Hydrolysis of 2-*Cyano*-2-*ethyl*cyclo*pentan*-1-*one.*

(1) 2-*Ethyl*cyclo*pentan*-1-*one* (XXII, p. 689).—This substance is prepared by boiling 5 grams of 2-cyano-2-ethyl*cyclo*pentan-1-one with 100 c.c. of 10 per cent. sulphuric acid under reflux for six hours and then distilling the product in a current of steam. A mobile oil is obtained which distils at 149°/756 mm.:

0·1940 gave 0·5330 CO_2 and 0·1890 H_2O. C = 74·92; H = 10·83.
$C_7H_{12}O$ requires C = 75·0; H = 10·7 per cent.

The ketone is soluble in about 15 parts of cold water.

The *semicarbazone*, $C_8H_{15}ON_3$, crystallises from alcohol in feathery needles melting at 177°:

0·1943 gave 0·4032 CO_2 and 0·1574 H_2O. C = 56·58; H = 9·00.
$C_8H_{15}ON_3$ requires C = 56·8; H = 8·9 per cent.

(2) δ-*Cyanoheptoic Acid*, $CN\cdot CHEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$.—2-Cyano-2-ethyl*cyclo*pentan-1-one is at once hydrolysed by alcoholic potash, yielding the above acid; the conditions are as follows.

Five grams of the keto-nitrile are added to an alcoholic solution containing the calculated quantity of potash, when much heat is generated and the solution becomes light brown. The alcohol is evaporated, and the solution, after diluting and acidifying, extracted with ether. The ethereal extract yields the acid as a viscid oil which does not show any tendency to crystallise:

0·1837 gave 0·4156 CO_2 and 0·1373 H_2O. C = 61·70; H = 8·30.
$C_8H_{13}O_2N$ requires C = 61·9; H = 8·4 per cent.

The *silver* salt, $C_8H_{12}O_2NAg$, is obtained as a white, crystalline precipitate on adding the calculated quantity of silver nitrate solution to a neutral solution of the ammonium salt of the acid. It rapidly darkens on exposure to light:

0·2372 gave 0·0973 Ag. Ag = 41·02.
$C_8H_{12}O_2NAg$ requires Ag = 41·2 per cent.

The further action of aqueous potassium hydroxide on δ-cyanoheptoic acid causes the evolution of ammonia, and if the action is continued until the evolution has ceased, the solution on acidifying and extracting with ether yields α-ethyladipic acid,

$$CO_2H{\cdot}CHEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

melting at 49° (compare Lean and Lees, Trans., 1897, **71**, 1067):

0·1853 gave 0·3734 CO_2 and 0·1374 H_2O. C = 54·95; H = 8·24.

$C_8H_{14}O_4$ requires C = 55·1; H = 8·0 per cent.

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LXXXIII.—*Nitrosoacetylamino-derivatives of the Benzene and Diphenyl Series.*

By JOHN CANNELL CAIN.

IN a recent paper (Trans., 1908, **93**, 681) was described the isolation of two solid modifications of *p*-nitrosoacetanilide, namely, the green, unimolecular and the white, bimolecular forms. As this seemed to be the first case of its kind, it appeared to be of interest to prepare other similar nitrosoacetylamino-compounds with the object of ascertaining if another pair of isomerides could be obtained. Accordingly, corresponding nitroso-compounds derived from toluene and chlorobenzene have been prepared, and, in addition, the analogous derivatives of diphenyl and ditolyl. In no case, however, has the existence of more than one form of nitroso-compound been observed, and hence the former instance must still be regarded as unique.

All the nitroso-compounds described in this paper were prepared by oxidising the corresponding amino-compounds with Caro's acid by the method already described in detail (*loc. cit.*), and they all give the usual reactions of the nitroso-group.

For the preparation of the diphenyl and ditolyl derivatives, the corresponding amino-compounds are very conveniently obtained by acetylating benzidine or tolidine in aqueous-alcoholic solution with acetic anhydride. The monoacetyl derivative of tolidine has not previously been described, whilst monoacetylbenzidine has only been isolated in very small amount in the preparation of the diacetyl derivative. It would seem, therefore, that this method may be of some value for the preparation of monoacetyl derivatives of the diamines of the diphenyl series.

EXPERIMENTAL.

2-*Nitrosoaceto*-p-*toluidide*, $NO \cdot C_6H_3Me \cdot NHAc$.

This was prepared from 4-acetylamino-*o*-toluidine (a solution of which was obtained by acetylating 2:4-tolylenediamine), and separates from alcohol in pale yellowish-brown crystals, melting at 195° to a yellowish-brown liquid. It dissolves in glacial acetic acid, giving a pale yellow solution, and is insoluble in benzene or water:

0·091 gave 12·4 c.c. N_2 at 17·5° and 756 mm. N = 16·01.

$C_9H_{10}O_2N_2$ requires N = 15·71 per cent.

Some attempts were made to prepare a monoacetyl compound from 2:5-tolylenediamine dihydrochloride. On boiling this substance with acetic acid and one molecular proportion of sodium acetate, or on adding acetic anhydride to an aqueous solution of the salt mixed with the same proportion of sodium acetate, a deep purple solution was obtained, from which a pure compound could not be isolated. On the other hand, acetylation of the free base in aqueous solution by means of acetic anhydride gives rise to the diacetyl compound, which is not hydrolysed by cold ammonia solution or by hot aqueous barium hydroxide. On boiling the aqueous solution with one molecular proportion of sodium hydroxide for several hours, hydrolysis indeed occurs, but apparently a mixture of the two possible monoacetyl compounds is formed. Further work in this direction was then abandoned, owing to the publication of patents in which both the desired compounds were described as having been obtained by a different method.

6-*Nitrosoaceto*-m-*toluidide*, $NO \cdot C_6H_3Me \cdot NHAc$.

This was prepared from 5-acetylamino-*o*-toluidine (Fr. Pat. 388454), and crystallises from alcohol in aggregates of green needles melting at 128—129°. It is sparingly soluble in ether, but readily so in glacial acetic acid:

0·1325 gave 17·9 c.c. N_2 at 17° and 760 mm. N = 15·98.

$C_9H_{10}O_2N_2$ requires N = 15·71 per cent.

5-*Nitrosoaceto*-o-*toluidide*, $NO \cdot C_6H_3Me \cdot NHAc$.

This was prepared from 6-acetylamino-*m*-toluidine (compare D.R.-P. 205037). It is sparingly soluble in ether, and crystallises from alcohol in long, flattened, green needles melting at 135—136°:

0·1326 gave 18·4 c.c. N_2 at 21·5° and 750 mm. N = 15·95.

$C_9H_{10}O_2N_2$ requires N = 15·71 per cent.

2-*Chloro-4-aminoacetanilide*, $NH_2·C_6H_3Cl·NHAc$.

The starting point for the preparation of a chloronitrosoacetanilide was 2-chloro-4-nitroaniline, which was acetylated as described by Cohn (*Mitt. Technol. Gewerb-Mus. Wien.*, 1902, [ii], **11**, 205), and the acetyl derivative, on reduction with iron powder and a few drops of acetic acid, yielded 2-*chloro-4-aminoacetanilide*, which crystallises from water in pale yellow plates melting at 111°:

0·1660 gave 21·3 c.c. N_2 at 19° and 754 mm. N = 14·95.
$C_8H_9ON_2Cl$ requires N = 15·18 per cent.

2-*Chloro-4-nitrosoacetanilide*, $NO·C_6H_3Cl·NHAc$.

On oxidising the base just described with Caro's acid, this compound is formed. It is soluble in alcohol, and sparingly so in hot water, from which it separates on cooling in green needles melting at 112—113°:

0·1205 gave 0·08532 AgCl. Cl = 17·50.
$C_8H_7O_2N_2Cl$ requires Cl = 17·86 per cent.

3 : 3′-*Dichloro-4 : 4′-diacetyldiaminoazobenzene*,
$NHAc·C_6H_3Cl·N_2·C_6H_3Cl·NHAc$.

In the above reaction was also formed a small quantity of this azo-compound, which is insoluble in alcohol and crystallises from glacial acetic acid in microscopic, pale yellow needles melting at 280°:

0·0434 gave 5·5 c.c. N_2 at 17° and 770 mm. N = 15·18.
$C_{16}H_{14}O_2N_4Cl_2$ requires N = 15·34 per cent.

Preparation of Monoacetyl-benzidine and -tolidine.

Of the common diamines of the diphenyl series, the only monoacetyl derivative which has hitherto been prepared is that of benzidine, but it was isolated only in very small amount as a by-product in the preparation of the diacetyl derivative by heating benzidine with glacial acetic acid (Schmidt and Schultz, *Ber.*, 1879, **12**, 489). A much more convenient method of obtaining this and the corresponding derivatives of other diamines is to carry out the acetylation by means of acetic anhydride in aqueous-alcoholic solution. In this way, a large proportion of the base is converted into the monoacetyl derivative, the proportion of monoacetyl to diacetyl compound being roughly, in the case of benzidine, 100 : 53, and in the case of tolidine, 100 : 35.*

Monoacetylbenzidine.—Benzidine (9·2 grams) is dissolved in hot dilute alcohol, the solution cooled, and acetic anhydride (5·2 grams) added. The solution is neutralised with ammonia, filtered hot (the residue is diacetylbenzidine), and water added until a turbidity is produced, when, on cooling, monoacetylbenzidine crystallises out.

Monoacetyltolidine, $NHAc\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2,H_2O$.—For the preparation of this compound an equivalent amount of tolidine is treated as just described.

Monoacetyltolidine crystallises from water in white, shining plates, which contain one molecule of water of crystallisation and melt at 103°:

0·1491 gave 13·1 c.c. N_2 at 20·5° and 760 mm. N = 10·27.

$C_{16}H_{18}ON_2,H_2O$ requires N = 10·28 per cent.

This substance is rather remarkable in that the acetyl group is very readily eliminated; even when recrystallised from water, some tolidine is formed, and the elements of acetic acid are expelled at 100°:

0·2578 lost 0·0538. Loss = 20·86.

$C_{16}H_{18}ON_2,H_2O$ requires $C_2H_4O_2 = 22{\cdot}05$ per cent.

That the substance was not merely tolidine acetate was proved by dissolving it in hydrochloric acid, rendering the solution alkaline with sodium carbonate, and crystallising the precipitate from water, when the original compound was again obtained in white, shining plates melting at 103°. Its constitution is also confirmed by the preparation from it of the nitroso-compound described later.

4-*Nitroso*-4′-*acetylaminodiphenyl*, $NO\cdot C_6H_4\cdot C_6H_4\cdot NHAc$.—This compound, prepared from monoacetylbenzidine, crystallises from alcohol in yellowish-brown, feathery needles, which darken at 200° and are completely melted at 275°. Its solution in glacial acetic acid is yellow:

0·1306 gave 12·8 c.c. N_2 at 22·5° and 761 mm. N = 11·40.

$C_{14}H_{12}O_2N_2$ requires N = 11·66 per cent.

4-*Nitroso*-4′-*acetylamino*-3 : 3′-*ditolyl*, $NO\cdot C_6H_3Me\cdot C_6H_3Me\cdot NHAc$.—This compound was prepared from monoacetyltolidine, and crystallises from alcohol in pale brown crusts melting at 154—155°. It is sparingly soluble in ether, but readily so in glacial acetic acid; the solutions are pale yellow:

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* In the case of dianisidine, no diacetyl derivative is formed under the same conditions.

0·1192 gave 10·6 c.c. N_2 at 19° and 764 mm. N = 10·50.
$C_{16}H_{16}O_2N_2$ requires N = 10·44 per cent.

My thanks are due to the Badische Anilin- und Soda-Fabrik for kindly sending me a specimen of 6-acetylamino-*m*-toluidine, to the Farbenfabriken vorm. F. Bayer & Co., for the 5-acetylamino-*o*-toluidine, and to Messrs. L. Cassella & Co., for the 2-chloro-4-nitroaniline.

I also take this opportunity of expressing my thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation, and also to Sir William Ramsay, K.C.B., for permission to carry out the work at University College.

UNIVERSITY COLLEGE,
LONDON.

LXXXIV.—*The Relation between the Strength of Acids and Bases and the Quantitative Distribution of Affinity in the Molecule.*

By BERNHARD FLÜRSCHEIM.

"NEGATIVE" radicles, that is, radicles which preferably dissociate as anions, generally raise the dissociation constant of an acid and reduce that of a base, whereas "positive" radicles have the opposite effect. In a number of cases, however, the reverse has been observed. To explain these apparent exceptions, various authors have suggested hypotheses differing from compound to compound and inapplicable to other cases.

A general theory of these phenomena can, however, only be formulated if, besides the polar character of substituents hitherto alone taken into consideration, attention is also paid to the amount of affinity which the linking of a substituent requires. An attempt to formulate such a general theory is made in this paper, and it may be observed that the views put forward do not necessitate any special conception concerning the nature of chemical affinity beyond the negative one, that atoms are not linked together by the interposition of electrons.

In order to make the subsequent deductions more intelligible, it may be well first to convey a clear idea of the factors which determine the strength of a chemical bond. Vorländer (*Annalen*, 1902, **320**, 110) stated that "the radicles have a double nature, which, on the one hand, corresponds to the positive and negative nature of the elements, and, on the other, to the saturated and unsaturated state."

The present author has shown (*J. pr. Chem.*, 1905, [ii], **71**, 500; 1907, **76**, 200; *Ber.*, 1906, **39**, 2016) that the strength of a chemical bond is a function of the disposable amounts of chemical force in the atoms which combine, and also of the polar nature of that force, and that the rate at which a bond is formed depends partly on both these factors. Later, Werner has adopted the same view regarding the affinity values of atomic linkings (*Chem. News*, 1907, **96**, 131). Recently (*Annalen*, 1908, **363**, 21; *Amer. Chem. J.*, 1909, **41**, 119), Michael has formulated a similar idea, and the resultant of the above two factors has been termed "chemical potential" by Michael and "affinergy" by Hibbert (Proc., 1909, **25**, 57).

In addition, Werner (*loc. cit.*) has pointed out, as a deduction from the above views, that elements which take a middle position between metals and non-metals, such as carbon and hydrogen, when combining with other elements saturate amounts of affinity practically independent of the polar nature of the latter elements; that, on the other hand, the strength of linking between elements of electrochemically more decided character greatly depends on their polarity, only small amounts of affinity being saturated in the case of allied elements, and vice versa.

Extending these views now a little further, it is clear that the most polar element is an electron; between the electron and hydrogen there exists therefore the fundamental difference that the strength of the former's bond with an atom mainly depends on the atom's polarity, whilst this factor hardly affects the strength of the bond between hydrogen and another atom.

The application of these fundamental conceptions to the subject of the present paper gives rise to the following deductions.

1. *Acids.*—The constant of the equilibrium:

$$\mathrm{R{\cdot}CO{\cdot}OH} \rightleftharpoons (\mathrm{R{\cdot}CO{\cdot}O} \;.\;.\;.\;.\; \ominus) + (\mathrm{H} \;.\;.\;.\;.\; \oplus)$$

(the dualistic theory of electricity is used for convenient graphical representation) depends, for the same solvent, on two factors, namely: (*a*) the dissociation constant is directly proportional to the force with which the negative electron adheres to the acidic radicle. This force mainly depends on the polar nature of the acidic radicle, which again is determined by the polar nature of the substituents; the more negative these are the greater that force becomes (polar factor).

(*b*) The dissociation constant is inversely proportional to the force with which hydrogen is linked to the acidic radicle. This chiefly depends on the amount of affinity which the atom to which hydrogen is linked can place at the latter's disposal. This amount is variable and depends on the force with which the substituents are linked to the molecule, and on their position (quantitative factor).

Claus has shown (*Ber.*, 1881, **14**, 432) that the force with which two atoms are linked is not a constant, but that, depending on the nature of the other atoms in the molecule, it must be assumed to vary from compound to compound. Later, Werner pointed out (*Vierteljahrschr. Züricher. Naturf. Gesellsch.*, 1891) that substitution in aliphatic acids takes place in the position α-, because the carbonyl-oxygen absorbs much of the carbonyl-carbon atom's affinity, which therefore can but weakly bind the carbon atom, thus leaving free affinity in the latter, by which substituents are attracted. The present author has shown (*J. pr. Chem.*, 1902, [ii], **66**, 321; *ibid.*, 1905, **71**, 497; 1907, **76**, 165 and 185) that unsaturated atoms, when directly linked to the benzene nucleus, cause substitution in the ortho- and para-positions, since their unsaturated nature enables them to bind the benzenoid carbon atom more strongly than hydrogen would, whereby the affinity which that carbon atom can place at the disposal of the ortho- and para-carbon atoms is reduced in amount, thus increasing the free affinity of the latter atoms; this again causes substituting molecules to be attracted by them, with the result that ortho- and para-disubstituted compounds are formed.

These views may be applied to the determination of the distribution of affinity in acids; if we have, for example, an unsaturated atom substituting hydrogen in the α-position, the carbon atom will be more strongly bound by it; this leads to a reduction of the force with which the α-atom binds the carbonyl-carbon atom, to a stronger linking between the latter and oxygen, and therefore to a weakening of the bond between oxygen and hydrogen. The following examples illustrate this case.

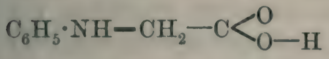
Although aniline is a base, anilinoacetic acid ($100\ k = 0{\cdot}0038$) is stronger than acetic acid ($100\ k = 0{\cdot}0018$) (Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 189).

α-Anilinopropionic acid ($100\ k = 0{\cdot}0022$) is stronger than propionic acid ($100\ k = 0{\cdot}0013$); α-anilino*iso*butyric acid ($100\ k = 0{\cdot}0036$) is stronger than *iso*butyric acid ($100\ k = 0{\cdot}0014$).

On the other hand, an unsaturated atom substituting hydrogen in the β-position must have exactly the opposite effect; it takes up a greater amount of the affinity of the β-carbon than does hydrogen; the amount of affinity with which the β-carbon can bind the α-carbon is thereby lessened, the strength of the linking between the latter and the carbonyl-carbon is increased, that between the latter and oxygen diminished, and the bond between oxygen and hydrogen is strengthened.

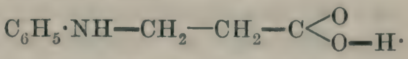
β-Anilinopropionic acid ($100\ k = 0{\cdot}0004$) is weaker than propionic acid (100 $k = 0{\cdot}0013$); β-anilino*iso*butyric acid (100 $k = 0{\cdot}0003$) is weaker than *iso*butyric acid (100 $k = 0{\cdot}0014$).

Graphically, linkings strengthened by the substituent may be represented by thick lines, and those which are weakened, by thin ones:



$C_6H_5{\cdot}NH-CH_2-C\Big\langle\begin{matrix}O\\O-H\end{matrix}$

and

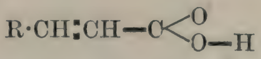


$C_6H_5{\cdot}NH-CH_2-CH_2-C\Big\langle\begin{matrix}O\\O-H\end{matrix}$.

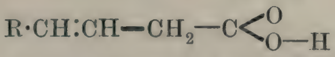
α-, β-, and $\gamma\delta$-Unsaturated acids are weaker than $\beta\gamma$-unsaturated acids, notwithstanding that in the $\alpha\beta$-acid the negative double linking is nearest the carboxyl group, as is shown by the following figures (Fichter and Pfister, *Annalen*, 1904, **334**, 203):

	k.		k.
Valeric acid	0·00161	n-Hexoic acid	0·00146
$\alpha\beta$-Pentenoic acid ...	0·00148	$\alpha\beta$-Hexenoic acid ...	0·00189
$\beta\gamma$-Pentenoic ,, ...	0·00335	$\beta\gamma$-Hexenoic ,, ...	0·00264
$\gamma\delta$-Pentenoic ,, ...	0·00209	$\gamma\delta$-Hexenoic ,, ...	0·00174
		$\delta\epsilon$-Hexenoic ,, ...	0·00191

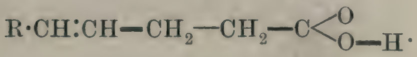
Here we have:



$R{\cdot}CH{:}CH-C\Big\langle\begin{matrix}O\\O-H\end{matrix}$

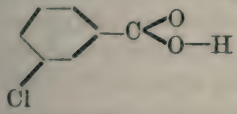


$R{\cdot}CH{:}CH-CH_2-C\Big\langle\begin{matrix}O\\O-H\end{matrix}$

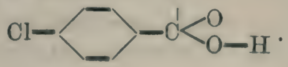


$R{\cdot}CH{:}CH-CH_2-CH_2-C\Big\langle\begin{matrix}O\\O-H\end{matrix}$.

m-Chloro- and bromo-benzoic acids are stronger than the para-isomerides, notwithstanding that usually the influence of a para-substituent is greater than that of a meta-. The explanation is again that the halogens, being unsaturated when univalent (which leads to their directing to the ortho- and para-positions), bind the benzene-carbon atom more strongly than hydrogen:



and

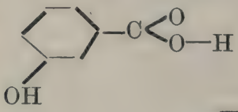


In the meta-acid, therefore, the quantitative influence of chlorine supports its polar effect, whereas in the para-acid the quantitative and polar factors work in opposite directions.

If the polar effect becomes less pronounced than is the case with the halogens, whilst the quantitative factor remains of the same order or even becomes stronger, it can be foreseen that cases must arise where the quantitative factor will mask the polar one, so that, for instance, a negative substituent may either raise or lower the constant, according to its quantitative effect, that is, according to its position. For this the groups $\cdot OH$ and $\cdot O{\cdot}CO{\cdot}CH_3$ furnish examples: m-hydroxybenzoic acid (100 $k = 0{\cdot}0087$) is stronger than benzoic acid (100 $k = 0{\cdot}0060$), whereas p-hydroxybenzoic acid (100 $k = 0{\cdot}00286$) is weaker; in the same way, *m*-acetoxybenzoic acid (100 $k = 0{\cdot}0099$) and *m*-acetylaminobenzoic acid (100 $k = 0{\cdot}0085$) are stronger than benzoic acid, whereas the para-isomerides are weaker (100 $k = 0{\cdot}0042$ and 0·0052 respectively) (Ostwald, *loc. cit.*).

o- and *p*-Hydroxycinnamic acids (100 $k = 0{\cdot}0021$ for both) are weaker than cinnamic acid (100 $k = 0{\cdot}0035$), and *op*-dihydroxycinnamic acid (100 $k = 0{\cdot}00188$) is still weaker (Ostwald, *loc. cit.*).

Graphically, the influence of the substituents on the strength of the various linkings can again be expressed thus:



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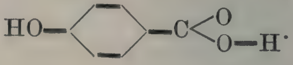
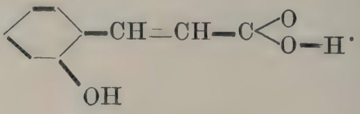




2. *Bases.*—(a) *Quaternary Ammonium Hydroxides and Analogous Derivatives of Oxygen, Iodine, Sulphur, Tin, etc.*

These may be subdivided into three classes:

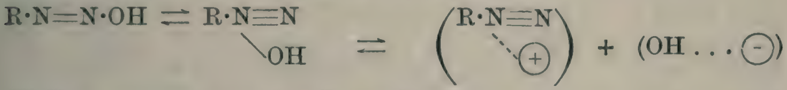
(i) Those which undergo thermic dissociation (but no intramolecular rearrangement) at a comparatively low temperature, and the central atom of which (nitrogen, etc.) therefore is linked to more atoms than it can retain in a stable condition. Ammonium, iodonium, sulphonium, phosphonium, arsonium, stilbonium, and selenonium hydroxides belong to this class. The central atom being oversaturated, it can but weakly retain the hydroxyl group, which accordingly easily undergoes electrolytic dissociation; thus tetramethylammonium hydroxide is a base comparable with the alkalis, because, for instance, its fluoride dissociates into methyl fluoride and trimethylamine at 180° in a vacuum.

Even distinctly negative substitution does not affect the strength of these bases, as is proved by the case of diphenyliodonium hydroxide, triphenylalkylphosphonium hydroxide, naphthyltrimethylammonium hydroxide, and many others.

(ii) Those which do not undergo thermic dissociation even at an elevated temperature, and the central atom of which can therefore firmly retain all the atoms to which it is linked, as, for example, the compounds $OH{\cdot}Hg{\cdot}OEt$ and $OH{\cdot}SnEt_3$. The linking between hydroxyl and the central atom not being a weak one, electrolytic dissociation does not take place readily; these compounds are therefore weak bases (Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 303). Trimethylplatinic hydroxide

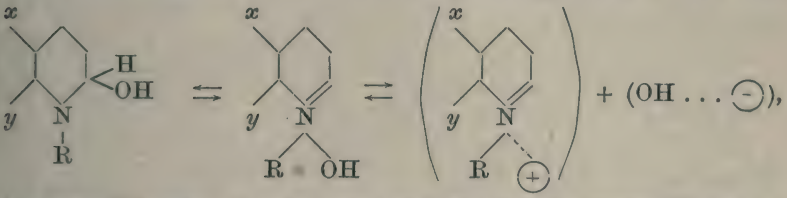
(Pope and Peachey, Proc., 1907, **23**, 86) also seems to belong to this class.

(iii) Those which undergo intramolecular rearrangement. Diazonium, oxonium, and azonium hydroxides belong to this class. From the investigations of Hantzsch (see below), Kehrmann (numerous publications), Decker (*Annalen*, 1909, **364**, 6, etc.), and others, the conclusion may be drawn that in the equilibria

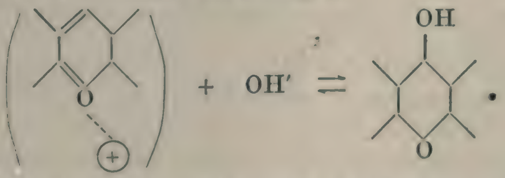


$$R\cdot N{=}N\cdot OH \rightleftharpoons \underset{\diagdown OH}{R\cdot N{\equiv}N} \rightleftharpoons \left(\underset{\oplus}{R\cdot N{\equiv}N}\right) + (OH\ldots\ominus)$$

(or in the corresponding, equally well applicable, formulæ of Cain) and



in the middle phase, the undissociated quaternary hydroxide, has no more real existence than in the case of amines (see below), that is, that all these hydroxides, as well as those derived from the amine bases, are of alkaline strength. If they do not generally appear to be so, it is simply because intramolecular rearrangement and thermic dissociation respectively are shifting the electrolytic equilibrium toward the left. The view of Hantzsch, that benzenediazonium hydroxide is weaker than the alkalis, and that of Decker, that some quaternary oxonium salts are partly hydrolysed to oxonium hydroxide, are not in agreement with the views advanced here, and are not a necessary conclusion from observed facts. If even the salts of oxonium bases can to some extent undergo intramolecular rearrangement, it should be rather due to a direct rearrangement of the cation, through the action of the hydroxyl ions of water, and without intermediate formation of the hypothetical undissociated oxonium hydroxide. Acids, by reducing the concentration of hydroxyl ions, of course counteract this change:



(iv) Those forming salts which suffer thermic dissociation in solution at the ordinary temperature. A number of these have been discovered by v. Halban (*Ber.*, 1908, **41**, 2417) and by Wedekind

(*Ber.*, 1908, **41**, 2659; 1909, **42**, 303). This change is shown by some quaternary ammonium salts containing both the phenyl and benzyl groups attached to nitrogen. As it occurs readily in non-dissociating solvents, more slowly or not at all in dissociating solvents, it must be produced by the non-dissociated salt. This thermic dissociation does not differ in principle from that shown by all ammonium salts at a somewhat higher temperature. The ease with which it takes place is proportional to the negativity of the substituents, which lowers the polar affinity between nitrogen and halogen, but still more to the quantitative absorption of the nitrogen's affinity by substituents, whereby its capacity of binding as many as five groups is lessened. The following constants for the rate of thermic dissociation in chloroform illustrate this:

Benzylphenylmethylallylammonium bromide, at 35°: $k = 0{\cdot}000674$.

Benzylphenyldiethylammonium bromide, at 35°: $k = 0{\cdot}00204$.

In alcohol or water no change even at 45°.

Phenylbenzylmethyl-[methylphenylaminoethyl]-ammonium bromide undergoes this change even in alcoholic solution at 18°; the rate in a mixture of chloroform and alcohol is considerably higher than that of the above compounds. Graphically, we have:

$C_7H_7{\cdot}NBrPhEt_2$
(Middle rate.)

$CH_2{:}CH{-}CH{-}NBrMePh{\cdot}C_7H_7$
(Lower rate.)

$PhMeN{-}NBrMePh{\cdot}C_7H_7$.
(Higher rate.)

With allyl and bromine, therefore, the quantitative factor prevails over the polar one; with allyl and an electron (which is much more polar than halogen) the electropolar influence must be expected to prevail; and actually allylamine ($100\,k = 5{\cdot}7 \times 10^{-3}$) as ion undergoes thermic dissociation more readily than propylamine ($100\,k = 4{\cdot}7 \times 10^{-2}$).

(b) *Amines.*—Hantzsch has shown, partly in conjunction with Davidson and Engler (*Ber.*, 1898, **31**, 340, 1612; 1900, **33**, 2147), that in the equilibrium

$$R{\cdot}NH_2 + H_2O \rightleftharpoons R{\cdot}NH_3{\cdot}OH \rightleftharpoons (R{\cdot}NH_3 \ldots \oplus) + OH'$$

the middle phase has no real existence.

The equilibrium can therefore be written:

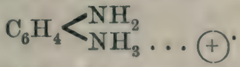
$$R{\cdot}NH_2 + (H \ldots \oplus) \rightleftharpoons (R{\cdot}NH_3 \ldots \oplus),$$

and it is shifted the more towards the left, that is, in the direction of hydrolysis, (i) the more negative the substituents are, since they proportionally lower the polar affinity between nitrogen and the positive electron; thus the nitroanilines and halogen-substituted anilines are all weaker than aniline.

(ii) the more the nitrogen's affinity is absorbed by substituents since its capacity of additionally binding a hydrogen atom and an electron is correspondingly lowered.

Thus hydrazine is a weaker monoacidic base than ammonia (Bredig, *loc. cit.*), since the tervalent nitrogen of each amino-group partly neutralises the residual affinity of the other: $(NH_2{-}NH_3 \ldots \oplus)$.

o-Phenylenediamine is a weaker monoacidic base than aniline:



$$C_6H_4 \begin{smallmatrix} \diagup NH_2 \\ \diagdown NH_3 \ldots \oplus \end{smallmatrix}.$$

(c) *Alkalis.*—Where a hydroxide does not undergo thermic dissociation and the hydroxyl group is therefore stably bound, a base can only be strong if this weakening factor is counteracted by a very pronounced positive polarity of the central atom, whereby the latter's polar affinity for the positive electron is increased. This explains why both thermally non-dissociating hydroxides of strongly positive metals (alkalis, etc.), and also thermally dissociating hydroxides of non-positive radicles (diphenyliodonium, diazonium, etc.), are strong bases, whereas thermally non-dissociating hydroxides of only moderately positive radicles (zinc, cadmium, trialkylstannic, etc.) are not.

3. *The Influence of Steric Hindrance on the Strength of Acids and Bases.*

Besides the two factors mentioned above, a third one must in many cases be taken into consideration, namely, steric hindrance. In the reversible reactions:

$$R{\cdot}CO{\cdot}OH \rightleftharpoons (R{\cdot}CO{\cdot}O \ldots \ominus) + (H \ldots \oplus)$$

and

$$(R{\cdot}NH_3 \ldots \oplus) \rightleftharpoons R{\cdot}NH_2 + (H \ldots \oplus)$$

steric hindrance must affect less the velocity from left to right than from right to left; for, apart from the electrons, the reaction from left to right is unimolecular, that from right to left bimolecular. In consequence, the equilibrium in both cases is, through steric hindrance, shifted towards the right, that is, the dissociation constant rises in the case of an acid and falls in that of an amine. This actually happens quite invariably.

Since, however, no substituent can exercise a steric influence without likewise making itself felt in a polar and quantitative way, it may be preferable to consider the steric effect in conjunction with the other two factors.

4. *Combination oj all Three Factors.*

A number of compounds has been cited in which no appreciable part falls to steric hindrance. These were meta- and para-substituted acids and certain unsaturated aliphatic acids. The quantitative and polar influence are, however, always simultaneously present, since all substituting atoms possess a different degree of saturation and a different state of electropolarity. It has been shown that these two factors may support or counteract each other, and that it is possible to foresee at a glance which of these two alternatives will take place. If the former, then the change in the dissociation constant will be found to lie in the direction assigned to it by the electropolar nature of the substituent, but to be more marked than this alone would lead one to expect (compare $\beta\gamma$-unsaturated acids); if the latter, it can be foreseen that marked unsaturation of the substituent must prevail over weak electropolarity, and vice versa (compare *p*-hydroxybenzoic acid, which is weaker than benzoic acid, and *p*-chlorobenzoic acid, which is stronger, etc., pp. 721, 722). The question as to which substituting atom is more and which less unsaturated is not subject to an arbitrary reply, but can be exactly ascertained from the relative directing power of the respective substituents when simultaneously present in the benzene nucleus; the substituent which prevails over the other possesses the greater amount of free affinity in the atom linked to the nucleus (compare previous papers, *loc. cit.*). As to the relative electropolarity of substituents, it may be fairly accurately determined by eliminating the quantitative factor in this way: in the meta- and para-isomerides of a substituted acid, for which steric hindrance hardly counts, the quantitative factor has opposite signs (compare pp. 721, 722). By adding the respective constants, it is therefore practically eliminated. The sums thus obtained represent the relative polarity of the substituents and may be applied to the analysis of ortho-substituted compounds, aliphatic and others. The following purely electropolar values have been calculated in this way, taking hydrogen ($2 \times k$ for benzoic acid) as a unit: $k_{\text{polar}} = \dfrac{k_{\text{meta}} + k_{\text{para}}}{2k_{\text{benzoic acid}}}$: $-NO_2 = 6{\cdot}2$; $-Cl = 2$; $-O{\cdot}CO{\cdot}CH_3 = 1{\cdot}2$; $-NH{\cdot}CO{\cdot}CH_3 = 1{\cdot}15$; $-CH_3 = 0{\cdot}85$; for $-OH = 1$ and $-NH_2 = 0{\cdot}25$, a small upward correction must be made, because the slight predominance of the quantitative influence in the para-position over that in the meta- (*loc. cit.*) makes itself most felt with these two most strongly linked groups.

The relative quantitative sequence can already be given as a first approximation; the definite sequence will only be available when experiments on the relative directing power in the benzene nucleus, which are in progress, will be completed:
$\cdot NH_2$, $\cdot NH(Alk)$, $\cdot NH(Ar)$, $\cdot N(Alk)_2$, $\cdot OH$, $\cdot O(Alk)$, $\cdot CH{:}CH\cdot$, $\cdot NHAc$, Cl, Br, I, Alk, $\cdot OAc$, H, $\cdot CH{:}O$, $\cdot C(Alk){:}O$, $\cdot C(OH){:}O$, $\cdot C{\vdots}N$, $\cdot NO_2$, $\cdot SO_3H$.*

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* It may be mentioned that the fact that $\cdot NH\cdot COR$ is linked much less strongly to the nucleus than $\cdot NH_2$, and $O\cdot CO\cdot CH_3$ less than OH, is explained by the hypo-

These considerations now make it possible to consider the effect of steric hindrance in detail. The relative sequence of steric effects is approximately known from the rate of acid esterification (compare Werner's *Manual of Stereochemistry* and numerous publications by Sudborough and others):

$$\cdot\mathrm{I} > \cdot\mathrm{Br},\ \cdot\mathrm{C_6H_5} > \cdot\mathrm{Cl},\ \cdot\mathrm{O},\ \cdot\mathrm{N},\ \cdot\mathrm{C}(\cdot\mathrm{CH_3},\ \cdot\mathrm{C}\text{ in carbonyl}) > \cdot\mathrm{H}\ ;$$
$$\text{ortho} > \beta > \alpha\ ;\ \text{and } \gamma,\ \delta,\ m,\ p,\ \text{side-chain in ortho} = \text{almost } 0\ ;$$

effect of second group in ortho, β, $\alpha >$ effect of first group.

The following typical cases (partly taken from the tables of Lundén, *Affinitatsmessungen*, Stuttgart, 1908) have been selected to show how an analysis of the magnitude of the three factors and their combination permits one to foresee the direction in which the affinity constant must be affected, even when all three factors are united in a substituent. The approximate effect on the constant is represented by + + + +, + + +, + +, +, and – – – –, – – –, – –, –, according to its magnitude and direction, *p* standing for polar, *q* for quantitative, and *s* for steric. By multiplication of the three effects, the direction of the change and the order of its magnitude can almost invariably be foreseen with an accuracy which, in the circumstances, must be considered very satisfactory. By giving each + or – the value of, say, 2, the total effect is obtained as the following example shows:

$$p++\ ;\ \ q-\ ;\ \ s+++\ ;\ \text{total } \frac{4\times 6}{2} = 12.$$

In the tables, total effects from 1 to 5 have been represented by + and – ; from 5 to 25 by + + and – – ; and over 25 by + + + and – – –. 0 expresses a very small or no effect, ? cases where the total foreseen effect equals 1, and where therefore the substituent should only exert a very small influence either way.

In estimating the quantitative factor, it must also be remembered that its influence decreases with the number of intervening atoms (*loc. cit.*), and that an equilibrium being established (*loc. cit.*), the strength of linkings is more affected by an unsaturated atom in the para- and ortho-positions than in the β-position of an aliphatic chain. Similarly, methyl-carbon acts as an unsaturated atom only when attached to an unsaturated atom (*loc. cit.*). In naphthalene the α-carbon is more unsaturated than the β- or a phenyl-carbon atom (*loc. cit.* For the formulation adopted for the primary and secondary nitro-groups, compare *J. pr. Chem.*, 1902, [ii], **66**, 16 and 321).

It will be noticed that among more than 100 compounds discussed in the tables and in the text, there is only one which shows a slight

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thesis of Brühl (*Ber.*, 1907, **40**, 896) and of Miss Smedley (Trans., 1909, **95**, 235) of a neutralisation of residual affinity between N and O, and O and O.

change in the wrong direction. This is β-naphthylacetylaminoacetic acid, which should be rather stronger than phenylacetylaminoacetic acid, but is slightly weaker. Since the constant of the latter acid, however, is too high when compared with all similar compounds, it is intended to determine it anew. Of all the constants of bases and monocarboxylic acids not mentioned in this paper, only the following —so far mainly estimated by a colorimetric method—were found to disagree: *m*-chloro- and *m*-bromo-aniline, *p*-chloro- and *p*-bromo-aniline, and *p*-aminophenol. These also will be measured by Farmer and Warth's method, and likewise triphenylacetic acid, which, although no constant is yet known, is described, without sufficient reason, as a very weak acid, whereas it should be very much stronger than acetic acid. It will then be further shown how the present theory is capable of throwing some additional light on other problems, such as the constitution and reaction of some triphenylcarbinol- and dibenzylidene-acetone derivatives, the configuration of isomeric ethylenic acids, the seeming discrepancy between the influence of alkyl substitution on the constants of malonic acid on the one hand and succinic acid on the other hand, etc. Lastly, it will be shown how, by a graphic method, the effects produced by the successive introduction of the same atom or group into acetic acid or ammonia can be even more accurately represented than by the simpler, but less elastic, method adopted in the table.

The experimental part of the present paper contains a crucial test in support of this theory. If merely considered from the electropolar point of view, the introduction of the basic phenylmethylamine group into the molecule of *m*-nitroaniline in the ortho-position with respect to the amino-group would result in an increase of the constant. By this theory, however, the result would be:

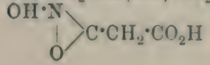
$$p++;\ q--;\ s---;\ \text{result}\ --.$$

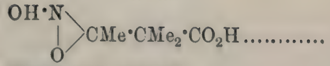
The observed result was a decrease of the constant k from 4×10^{-12} to 5×10^{-13} at 25°.

EXPERIMENTAL.

The preparation and properties of 4-nitro-2-amino-diphenylmethylamine, $C_6H_5\cdot NMe\cdot C_6H_3(NO_2)\cdot NH_2$, will be described in a paper on "the mechanism of the reduction of nitroanilines and nitrophenols."

The following measurements and calculations were carried out strictly according to Farmer and Warth's method (*loc. cit.*). q (see below) was, however, taken at 0·058, instead of 0·059, this value being determined by a special experiment.

Acid.	100 k_1.	Compared with	100 k_2.	p.	q.	s.	K_1/K_2 foreseen change.	K_1/K_2 observed.
$CH_2Me\cdot CO_2H$	0·0014 (average)	$Me\cdot CO_2H$	0·0018	– –	+	+	?	0·75
$CH_2Me\cdot CH_2\cdot CO_2H$	0·00158	$CH_2Me\cdot CO_2H$	0·0014	–	0	+ +	+	1·1
$CHMe_2\cdot CO_2H$	0·00144	$CH_2Me\cdot CO_2H$	0·0014	– –	+	+ +	+	1·02
$CHMeEt\cdot CO_2H$	0·0017	$CHMe_2\cdot CO_2H$	0·00144	–	0	+ +	+	1·2
$CHEt_2\cdot CO_2H$	0·00195 (average)	$CHMeEt\cdot CO_2H$	0·0017	–	0	+ + +	+	1·15
$CHMe_2\cdot CH_2\cdot CO_2H$	0·00173	$CH_2Et\cdot CO_2H$	0·00149	–	0	+ + +	+	1·15
$CHMeBr\cdot CO_2H$	0·108	$CH_2Me\cdot CO_2H$	0·0014	+ + +	+	+ +	+ + +	77·0
$CHMeCl\cdot CO_2H$	0·147	$CHMeBr\cdot CO_2H$	0·108	+	+	–	+	1·35
$CH_2Cl\cdot CH_2\cdot CO_2H$	0·00859	$CH_2Me\cdot CO_2H$	0·0014	+ +	–	+ +	+ +	6·5
$CH_2Br\cdot CH_2\cdot CO_2H$	0·0098	$CH_2Cl\cdot CH_2\cdot CO_2H$	0·00859	–	0	+ +	+	1·15
$CH_2I\cdot CH_2\cdot CO_2H$	0·0090	$CH_2Br\cdot CH_2\cdot CO_2H$	0·0098	–	0	+	?	0·9
$CH_2Cl\cdot[CH_2]_2\cdot CO_2H$	0·0030	$CH_3\cdot[CH_2]_2\cdot CO_2H$	0·00149	+	+	0	+	2·0
$CH_2Br\cdot[CH_2]_2\cdot CO_2H$	0·0026	$CH_2Cl[CH_2]_2\cdot CO_2H$	0·0030	–	0	0	–	0·85
$CH_2I\cdot[CH_2]_2\cdot CO_2H$	0·0023	$CH_2Br[CH_2]_2\cdot CO_2H$	0·0026	–	0	0	–	0·9
$CH_2Cl\cdot[CH_2]_3\cdot CO_2H$	0·00204	$CH_3[CH_2]_3\cdot CO_2H$	0·0016	+	0	0	+	1·25
$CH_2Br\cdot[CH_2]_3\cdot CO_2H$	0·00191	$CH_2Cl\cdot[CH_2]_3\cdot CO_2H$	0·00204	–	0	0	–	0·95
$CH_2I\cdot[CH_2]_3\cdot CO_2H$	0·00171	$CH_2Br\cdot[CH_2]_3\cdot CO_2H$	0·00191	–	0	0	–	0·9
$CN\cdot CH_2\cdot CO_2H$	0·37	$CH_3\cdot CO_2H$	0·0018	+ + + +	–	α + β + +	+ + +	200·0
$OH\cdot CH_2\cdot CO_2H$	0·0152	$CH_3\cdot CO_2H$	0·0018	+	+ + +	+	+ +	8·5
$OMe\cdot CH_2\cdot CO_2H$	0·0335	$OH\cdot CH_2\cdot CO_2H$	0·0152	–	–	+ +	?	2·2
$OEt\cdot CH_2\cdot CO_2H$	0·0234	$OMe\cdot CH_2\cdot CO_2H$	0·0335	–	–	0	–	0·7
$OPh\cdot CH_2\cdot CO_2H$	0·076	$OEt\cdot CH_2\cdot CO_2H$	0·0234	+ +	–	+ +	+ +	3·2
$OH\cdot CHMe\cdot CO_2H$	0·0138	$CH_2Me\cdot CO_2H$	0·00140	0	+ + +	+	+ +	9·9
$OH\cdot CH_2\cdot CH_2\cdot CO_2H$	0·00311	$CH_2Me\cdot CO_2H$	0·00140	+	– –	+ +	+	2·2
$OH\cdot CH_2\cdot[CH_2]_2\cdot CO_2H$	0·0019	$CH_2Me\cdot CH_2\cdot CO_2H$	0·00149	0	+	0	+	1·3
$OH\cdot CH_2\cdot CH(OH)\cdot CO_2H$	0·0228	$OH\cdot CHMe\cdot CO_2H$	0·0138	+	– –	+ +	+	1·6
	0·0162	$CH_2Me\cdot CO_2H$	0·00140	+ + +	– –	β 2 × + +	+ +	11·5

Acid.	100 k_1.	Compared with	100 k_2.	p.	q.	s.	K_1/K_2 foreseen change.	K_1/K_2 observed.
	0·0123	$C_2H_5\cdot CMe_2\cdot CO_2H$	0·00157	+ + +	− −	β 2 × + +	+ +	7·8
$NHPh\cdot CH_2\cdot CO_2H$	0·0038	$Me\cdot CO_2H$	0·0018	− − −	+ + + +	α + β + +	+ +	2·1
$NHPh\cdot CH_2\cdot CH_2\cdot CO_2H$	0·0004	$CH_2Me\cdot CO_2H$	0·00140	− −	− − − −	+ +	− −	0·3
$NHPh\cdot CHMe\cdot CO_2H$	0·0022	$CH_2Me\cdot CO_2H$	0·00140	− − −	+ + + +	α + β + +	+ +	1·6
$NHPh\cdot CMe_2\cdot CO_2H$	0·00367	$CHMe_2\cdot CO_2H$	0·00144	− − −	+ + + +	α + β + +	+ +	2·6
$NHPh\cdot CH_2\cdot CMe\cdot CO_2H$	0·0003	$CHMe_2\cdot CO_2H$	0·00144	− −	− − −	+ +	− −	0·2
$NHPh\cdot CHEt\cdot CO_2H$	0·00317	$CH_2Et\cdot CO_2H$	0·00149	− − −	+ + + +	α + β + +	+ +	2·1
$(\beta)\text{-}C_{10}H_7\cdot NH\cdot CH_2\cdot CO_2H$	0·0060	$NHPh\cdot CH_2\cdot CO_2H$	0·0038	+	0	+	+	1·6
$(\alpha)\text{-}C_{10}H_7\cdot NH\cdot CH_2\cdot CO_2H$	0·0040	$(\beta)\text{-}C_{10}H_7\cdot NH\cdot CH_2\cdot CO_2H$	0·0060	−	0	−	−	0·7
$NPh(CH_2\cdot CO_2H)_2$	0·027	$CH_2(CH_2\cdot CO_2H)_2$	0·004	− − −	+ + + +	β + +	+ +	6·7
$CHPh(CH_2\cdot CO_2H)_2$	0·0077	$CH_2(CH_2\cdot CO_2H)_2$	0·004	+	−	+ +	+	1·9
$CH_2Ph\cdot CO_2H$	0·0056	$Me\cdot CO_2H$	0·0018	+	+	+ +	+ +	3·1
$CH_2Ph\cdot CH_2\cdot CO_2H$	0·0023	$CH_2Me\cdot CO_2H$	0·0014	+	−	+ +	+	1·65
$OH\cdot CHPh\cdot CO_2H$	0·043	$OH\cdot CH_2\cdot CO_2H$	0·0152	+	+	+ +	+ +	2·8
$CMe(:NOH)\cdot CO_2H$	0·051	$CH_2Me\cdot CO_2H$	0 0014	+ + +	+ +	α + β + +	+ + +	36·0
$CH(:NOH)\cdot CH_2\cdot CO_2H$	0·0099	$CH_2Me\cdot CO_2H$	0·0014	+ +	−	+ +	+ +	7·0
$CH_3\cdot[CH_2]_2\cdot C(:NOH)\cdot CO_2H$	0·0685	$CH_3\cdot[CH_2]_3\cdot CO_2H$	0·0016	+ + +	+ +	α + β + +	+ + +	42·5
$CH_3\cdot C(:NOH)\cdot[CH_2]_2\cdot CO_2H$	0·0023	$CH_3\cdot[CH_2]_3\cdot CO_2H$	0·0016	+	+	0	+	1·4
$NPhAc\cdot CHMe\cdot CO_2H$	0·0125	$CH_2Me\cdot CO_2H$	0·0014	+	+	α + β + +	+ + +	8·9
$NPhAc\cdot CMe_2\cdot CO_2H$	0·0109	$CHMe_2\cdot CO_2H$	0·00144	+	+	α + β + +	+ + +	7·6
$NPhAc\cdot CH_2\cdot CMe\cdot CO_2H$	0·0029	$CHMe_2\cdot CO_2H$	0·00144	+	−	+ +	+	2·0
$(\beta)\text{-}C_{10}H_7\cdot NAc\cdot CH_2\cdot CO_2H$	0·024	$NPhAc\cdot CH_2\cdot CO_2H$	0·026	+	0	+	+	0·9

Acid.	100 k_1.	Compared with	100 k_2.	p.	q.	s.	k_1/K_2 foreseen change.	K_1/K_2 observed.
(α)-$C_{10}H_7$·NAc·CH_2·CO_2H	0·0207	(β)-$C_{10}H_7$·NAc·CH_2·CO_2H	0·024	0	–	0	–	0·85
(β)-$C_{10}H_7$·NAc·CH_2·CHMe·CO_2H	0·0022	NPhAc·CH_2·CHMe·CO_2H	0·0029	0	0	0	?	0·75
NHAc·CH_2·CO_2H	0·0230	CH_2Me·CO_2H	0·00140	+	+	α + β + +	+ + +	16·5
o-Chlorobenzoic	0·132	Benzoic	0·006	+ +	–	+ + +	+ +	22·0
o-Bromobenzoic	0·145	*o*-Chlorobenzoic	0·132	–	0	+ +	+	1·1
o-Iodobenzoic	0·137	,,	0·132	– –	0	+ + +	+	1·05
m-Chlorobenzoic	0·0155	Benzoic	0·006	+	+	0	+	2·6
m-Bromobenzoic	0·0137	*m*-Chlorobenzoic	0·0155	–	0	0	–	0·9
o-Hydroxybenzoic	0·102	Benzoic	0·006	+	–	+ + +	+ +	17·0
2 : 6-Dihydroxybenzoic	5·0	*o*-Hydroxybenzoic	0·102	+	–	+ + + +	+ +	49·0
p-Hydroxybenzoic	0·00286	Benzoic	0·006	0	– –	0	–	0·5
m-Hydroxybenzoic	0·0087	,,	0 006	0	+	0	+	1·45
o-Aminobenzoic	0·00106	,,	0·006	– – – –	– –	+ + +	– –	0·2
m-Aminobenzoic	0·00163	,,	0·006	– –	+	0	–	0·25
p-Aminobenzoic	0·00121	,,	0·006	– –	– – –	0	– –	0·2
o-Acetylaminobenzoic	0·0236	,,	0·006	+	–	+ + +	+ +	39·0
o-Nitrobenzoic	0·616	,,	0·006	+ + + +	+	+ + +	+ + +	103·0
m-Nitrobenzoic	0·0345	,,	0·006	+ +	–	0	+	5·75
p-Nitrobenzoic	0·04	,,	0·006	+ + +	+	0	+ +	6·65
o-Toluic	0·0120	,,	0·006	–	–	+ + +	+	2·0
o-Acetoxybenzoic	0·0333	,,	0·006	+ +	–	+ + +	+ +	5·6
Phthalic monomethyl ester	0·0656	,,	0·006	+ + +	+	+ + +	+ + +	11·0
,, monoethyl ,,	0·0551	Phthalic monomethyl ester	0·0656	0	–	0	–	0·85
o-Sulphoaminobenzoic	0·206	Benzoic	0·006	+ + + +	+	+ + + +	+ + +	34·5

Amine.	100 k_1.	Compared with	100 k_2.	p.	q.	s.	K_1/K_2 foreseen change.	K_1/K_2 observed.
$NHMe_2$	0·074	NH_2Me	0·05	+ + +	0		?	1·5
NMe_3	0·0074	$NHMe_2$	0·074	+ + +	0	– – – –	–	0·1
$NH_2{\cdot}CH_2Ph$	0·0024	NH_2Et	0·056	– –	+	– – –	– –	0·045
NH_2Pr^{α}	0·047	NH_2Et	0·056	+	0	– –	–	0·85
NH_2Pr^{β}	0·053	NH_2Et	0·056	+ +	0	– –	?	0·95
$NH_2{\cdot}CH_2{\cdot}CHMe_2$	0·031	NH_2Pr^{α}	0·047	+	0	– –	–	0·66
$NH_2{\cdot}CHMeEt$	0·044	NH_2Pr^{α}	0·047	+ +	0	– –	?	0·95
$NH(CH_2{\cdot}CH_2Me)_2$	0·102	$NHMe_2$	0·126	2 +	0	2 – –	–	0·8
$NH(CH_2Pr^{\beta})_2$	0·048	$NHPr^{\alpha}_2$	0·102	2 +	0	2 – –	–	0·45
$N(CH_2Pr^{\beta})_3$	0·026	NPr^{α}_3	0·055	3 +	0	3 – –	–	0·45
$N(CH_2{\cdot}CH_2Me)_3$	0·055	NEt_3	0·064	3 +	0	3 – –	–	0·85
o-Nitroaniline	1×10^{-12}	Aniline	$4·6 \times 10^{-8}$	– – – –	+	– – –	– – –	0·000022
m-Nitroaniline	4×10^{-10}	,,	$4·6 \times 10^{-8}$	– – –	–	0	– –	0·0085
p-Nitroaniline	1×10^{-10}	*m*-Nitroaniline	$4·0 \times 10^{-10}$	– –	+	0	–	0·25
o-Aminobenzoic acid	$1·38 \times 10^{-10}$	Aniline	$4·6 \times 10^{-8}$	– – – –	+	– – –	– – –	0·003
m-Aminobenzoic ,,	$1·23 \times 10^{-9}$	,,	$4·6 \times 10^{-8}$	– –	–	0	– –	0·027
p-Aminobenzoic ,,	$2·33 \times 10^{-10}$	*m*-Aminobenzoic acid	$1·23 \times 10^{-9}$	– –	+	0	–	0·18
o-Aminomethyl benzoate	$1·59 \times 10^{-10}$	*o*-Aminobenzoic acid	$1·38 \times 10^{-10}$	+	–	0	?	1·05
m-Aminomethyl benzoate	4×10^{-9}	*m*-Aminobenzoic acid	$1·23 \times 10^{-9}$	0	+	0	+	3·25
β-Naphthylamine	$1·9 \times 10^{-8}$	Aniline	$4·6 \times 10^{-8}$	–	0	0	–	0·4
α-Naphthylamine	$9·3 \times 10^{-9}$	*β*-Naphthylamine	$1·9 \times 10^{-8}$	0	–	–	–	0·5
o-Phenylenediamine	$3·1 \times 10^{-8}$	Aniline	$4·6 \times 10^{-8}$	+ + + +	– –	– – –	–	0·65
o-Toluidine	$3·3 \times 10^{-8}$	,,	$4·6 \times 10^{-8}$	+ +	–	– – –	–	0·7
m-Toluidine	6×10^{-8}	,,	$4·6 \times 10^{-8}$	+	+	0	+	1·3
p-Toluidine	2×10^{-7}	,,	$4·6 \times 10^{-8}$	+ +	–	0	+	4·35
p-Anisidine	$1·4 \times 10^{-7}$	,,	$4·6 \times 10^{-8}$	+	–	0	?	3·05
p-Aminoazobenzene	$8·9 \times 10^{-10}$	,,	$4·6 \times 10^{-8}$	–	– –	0	– –	0·02

First, the determination of the constant for *m*-nitroaniline was repeated, but at 17° instead of 25°. The letters signifying

c_1 = original concentration of the acid
c_2 = original concentration of base
c = concentration of base in aqueous layer
F = distribution-coefficient of base between benzene and water
q = volume of benzene for 1 litre of water
v = dilution in litres per gram-equivalent
x = degree of hydrolysis
k = dissociation constant
C_H = concentration of hydrogen ions of water;

the following were the results:

Used: substance = 1·2473 grams; benzene = 90 c.c.; water = 1500 c.c.; $t = 17°$.

Found: residue from 75 c.c. benzene = 0·6473 gram; $F = 26·1$.

Used: substance = 2·2293 grams; benzene = 90 c.c.; water (including acid) = 1500 c.c.; $t = 17°$.

N-HCl = 16·15 c.c. = 1 equivalent, calculated on base.

$C_{H(17^\circ)} = 0·77 \times 10^{-7}$; $c_1 = 0·01077$; $c_2 = 0·01077$; $v = 92·9$; $q = 0·058$.

Found: residue from 75 c.c. benzene = 0·5569 gram; $c = 0·00206$; $x = 0·339$; $k_{(17^\circ)} = 3·17 \times 10^{-12}$.

This is a good agreement with Farmer and Warth, who found

$$k_{(25^\circ)} = 4 \times 10^{-12}.$$

Nitroaminodiphenylmethylamine being practically insoluble in water, both the distribution-coefficient and the hydrolysis were not determined by evaporating the benzene layer, but by exhaustive extraction of the aqueous layer.

Used: substance = 0·8050 gram; benzene = 60 c.c.; water = 1000 c.c.; $t = 25°$.

Found: in aqueous layer = 0·0020 gram; $F = 6920$.

Used: substance = 0·6776 gram; benzene = 35 c.c.; water = 1200 c.c.; $t = 25°$.

Found: in aqueous layer = 0·0034 gram; $F = 6997$.

Used: substance = 0·6935 gram; benzene = 60 c.c.; water (including acid) = 1000 c.c.; $t = 25°$;

N-HCl = 114 c.c. = 40 equivalents, calculated on base.

$C_{H(25^\circ)} = 1·09 \times 10^{-7}$; $c_1 = 0·114$; $c_2 = 0·00285$; $v = 351$; $q = 0·058$.

Found: in aqueous layer = 0·0045 gram; $c = 0·000007$; $x = 0·902$;

$$k_{25^\circ} = 5·0 \times 10^{-13}.$$

q was thus determined: the above 0·8050 gram, which gave 0·0020 gram in the aqueous layer, also gave 0·6935 gram in 50 of the 60 c.c.

of benzene that had been used. From this, the total benzene layer is calculated at 58 c.c., or $q = 0{\cdot}058$.

In conclusion, the author wishes to thank Dr. Senter for his kind help in connexion with this paper.

FLEET,
HANTS.

LXXXV.—*The Constituents of the Rhizome of Apocynum androsaemifolium.*

By CHARLES WATSON MOORE.

UNDER the title of "Apocynum," the Pharmacopœia of the United States recognises "the dried rhizome of *Apocynum cannabinum*, Linné, or of closely allied species of *Apocynum*." In "Gray's *New Manual of Botany*," 1908, 7th ed., p. 662, only three species of *Apocynum* are described, namely, *A. androsaemifolium*, Linné, *A. mèdium*, Greene, which is similar in its characters to the preceding, and *A. cannabinum*, Linné. The last-mentioned species, however, is stated to vary greatly, and several varieties of the plant are regarded by some botanists as definite species, to which distinctive names have been assigned.

An investigation of material, described as the root of *Apocynum cannabinum*, L., was conducted some years ago by Schmiedeberg (*Arch. exp. Path. Pharm.*, 1883, **16**, 161), who obtained two products, designated as apocynin and apocynein, the latter having been regarded as a glucoside similar in character to saponin. Both these products were, however, only obtained in an amorphous state, and evidently consisted of mixtures.

Wood (*J. Amer. Med. Assoc.*, 1904, **43**, 1953) obtained from a fluid extract of *Apocynum cannabinum* a crystalline substance, m. p. 112°, which he believed to be identical with the so-called "crystalline apocynin" of commerce, but found the latter to be, physiologically, almost inert. The same investigator was "inclined to believe that the active principle is in the nature of a glucoside," but this opinion was based only on the observation that a solution which had been heated with an acid had thereby become deprived of its physiological activity. The present investigation has shown that the above view is incorrect, but that the active principle, which has now been obtained in a pure state, is decomposed on heating with acids, although it is not a glucoside.

Finnemore (Trans., 1908, **93**, 1513), in a publication entitled "The Constituents of Canadian Hemp, Part I," has recorded the isolation of a crystalline substance from the root (rhizome) of *Apocynum cannabinum*. This substance, which was described under the name of "apocynin"—having been found to correspond to the crystalline apocynin of commerce—he has shown to be identical with acetovanillone.

The present investigation of the rhizome of *Apocynum androsaemifolium*, Linné, commonly known as "Spreading Dogbane," has resulted in the isolation of its chief active constituent, which is designated *apocynamarin*, $C_{14}H_{18}O_3,H_2O$, m. p. 170—175°. This substance has an intensely bitter taste, and is highly toxic. The rhizome has, furthermore, been shown to contain a considerable proportion of acetovanillone, the glucoside of which, $CH_3{\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3){\cdot}O{\cdot}C_6H_{11}O_5$, m. p. 218—220°, has also been isolated, and designated *androsin*. A summary of the results of the complete investigation of the rhizome, in the course of which a number of other substances have been isolated, is given in a summary at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation was obtained from the United States, and was supplied as representing the "Apocynum" of the U.S. Pharmacopœia. It conformed in its anatomical characters to the description given of the rhizome of *Apocynum androsaemifolium*, Linné.

A portion of the material (25 grams) was tested for the presence of an alkaloid, but the reactions were so slight as to indicate that it contained not more than traces of such a substance.

Twenty grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 90—100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	1·19	grams	=	5·95	per cent.
Ether	,,	0·39	,,	=	1·95	,,
Chloroform	,,	0·09	,,	=	0·45	,,
Ethyl acetate	,,	0·24	,,	=	1·20	,,
Alcohol	,,	2·74	,,	=	13·70	,,
	Total	4·65	grams	=	23·25	per cent.

For the purpose of a complete examination, a quantity (39·92 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 10·48 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (5 kilograms) of the above-mentioned extract, representing about 19 kilograms of the rhizome, was mixed with water, and steam passed through the mixture for several hours. The distillate, which amounted to about 10 litres, contained some drops of oil floating on the surface. It was thoroughly extracted with ether, and the ethereal liquid shaken with a dilute solution of ammonium carbonate. On acidifying this alkaline liquid, a small quantity of an oily acid separated, which was removed by ether and distilled under the ordinary pressure, when it passed over between 210° and 215° as an almost colourless, viscid liquid, and amounted to about 2·0 grams. It was converted into the ammonium salt, from which five fractions of silver salt were precipitated. The analysis of these salts showed that the acid consisted chiefly of an octoic acid. The ethereal liquid which had been extracted with ammonium carbonate, as above described, was shaken with successive portions of a dilute solution of potassium hydroxide. The alkaline liquids thus obtained were united, acidified, and extracted with ether, when a small amount (1·2 grams) of a crystalline substance, melting at 112—114°, was obtained. This proved to be identical with a substance which was afterwards obtained in larger quantity, and was shown to be acetovanillone.

The ethereal liquid which had been extracted with potassium hydroxide, as above described, yielded, after removing the solvent, a small quantity of an essential oil, which distilled between 130° and 250°. It was a pale yellow liquid, possessing a strong persistent odour and the following constants: d 12°/12° = 0·948; α_D +0°50′ in a 1-dcm. tube. The amount of this essential oil was 3·0 grams. It gave a strong furfuraldehyde reaction.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as above described, there remained a quantity of a brown resin (*A*) and a dark-coloured aqueous liquid. The latter was separated by filtration while still hot, and the brown resin repeatedly treated with boiling water until nothing further was removed. The aqueous liquid and washings from the brown resin were united and kept for several days, when a quantity of a brown resin (*B*) slowly separated. This was removed from the liquid and thoroughly washed with cold water, the washings being added to the aqueous liquid, which may be designated as (*C*).

Examination of the Resin (A).

This resin, at the ordinary temperature, was a dark brown, sticky solid, and amounted to 1010 grams. It was first treated with a large volume of cold light petroleum (b. p. 35—50°), the undissolved material being allowed to deposit, and the clear liquid decanted, after which the same operation was repeated. The brown, undissolved residue was then further extracted in a Soxhlet apparatus with light petroleum, and the combined petroleum extracts concentrated as far as possible on the water-bath.

The portion of the resin (*A*) which was insoluble in light petroleum amounted to 368 grams, and formed a dark brown, amorphous powder. This was thoroughly extracted with alcohol in a Soxhlet apparatus, when 140 grams of it were dissolved. The remaining 228 grams consisted of a dark brown powder, which, although originally extracted from the rhizome by alcohol, had evidently suffered some change, and was now insoluble in all the usual solvents. The portion soluble in alcohol was mixed with purified sawdust, the thoroughly-dried mixture being then successively extracted in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin (A).

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

This extract was a dark-coloured, sticky solid, and amounted to 642 grams. It was dissolved in 4 litres of ether, and the solution allowed to stand for about ten days, when a grey, sparingly soluble substance separated. This was collected, washed with a little ether, and crystallised several times from dilute pyridine, when it formed tufts of colourless, microscopic needles melting at 285—290°:

0·1365 gave 0·3625 CO_2 and 0·1290 H_2O. C = 72·4; H = 10·5.

$C_{23}H_{40}O_4$ requires C = 72·6; H = 10·5 per cent.

The substance was thus shown to be identical with ipuranol, a dihydric alcohol which has recently been obtained in these laboratories from several plants. The amount of ipuranol obtained in the present instance was 1·5 grams. On boiling the substance with acetic anhydride, it yielded diacetylipuranol, which separated in colourless leaflets melting at 162°.

The ethereal solution, after the removal of the ipuranol as above described, was diluted with ether to about 8 litres, then shaken with successive portions of an aqueous solution of sodium carbonate, and finally washed with water. The alkaline liquids and washings were united and acidified, when a quantity of solid separated. On attempting to remove this by shaking with ether, an inseparable emulsion was formed. The acid liquid was therefore heated to boiling and cooled, after which the precipitated solid could easily be removed by filtration. The solid material so obtained was distilled under diminished pressure, when most of it passed over between 240° and 260°/25 mm. as a viscid, oily liquid which solidified on cooling. It amounted to 20 grams and consisted of a mixture of fatty acids, which were examined in connexion with a similar product obtained from the neutral portion of the petroleum extract after hydrolysis.

The aqueous liquid from which the above-described fatty acids had been separated yielded, on extraction with ether, about 1 gram of acetovanillone, melting at 112—114°.

Unsaponifiable Constituents of the Petroleum Extract.

The ethereal liquid which had been extracted with sodium carbonate, as above described, was subsequently shaken with a solution of sodium hydroxide, which, however, removed nothing. The ether was then evaporated, when a quantity of a sticky solid was obtained. This was boiled for five hours with an alcoholic solution of potassium hydroxide, the alcohol removed, and water added, when a quantity of amorphous, grey material was precipitated. This was separated by filtration, and well washed with boiling water, after which it was treated with ether, when nearly all of it dissolved. The ethereal solution was concentrated to 1500 c.c., when, after some time, small, colourless needles separated. These, when dry, weighed 200 grams. The material contained in the mother liquor yielded, after solution in dilute alcohol, a further 35 grams of this crystalline material. The final mother liquor contained 215 grams of uncrystallisable products, which will be referred to later.

The entire amount (235 grams) of the above-mentioned crystalline product was recrystallised from dilute alcohol, when nearly 200 grams of the material was obtained in small, colourless needles melting at 153—155°. One hundred grams of this crystallised product were subjected to a prolonged process of fractional crystallisation from ethyl acetate. A large number of fractions was thus obtained, which showed indefinite melting points, ranging from 151—155° to 180—185°. The specific rotatory power of these fractions also varied; thus the fraction melting at 180—185° had $[\alpha]_D + 31{\cdot}6°$, whilst the more soluble fraction, melting at 151—155°, had $[\alpha]_D + 54{\cdot}6°$. The percentage composition of the various fractions was uniform within the limits of experimental error; the mean of six analyses being $C = 83{\cdot}9$, $H = 11{\cdot}7$ per cent. From the results it was evident that the above-described crystalline product consisted of a mixture of substances of very similar composition, but all attempts to separate them by fractional crystallisation were unsuccessful. The entire mixture was therefore heated with acetic anhydride, after which the acetylated product was submitted to fractional crystallisation from ethyl acetate. Although by this means the separation was far from complete, the isolation of two pure substances was effected.

Isolation of a New Monohydric Alcohol, Androsterol, $C_{30}H_{49}\cdot OH$.

One hundred grams of the above-mentioned acetylated product were repeatedly crystallised from ethyl acetate, when a small fraction (5 grams) was eventually obtained, which melted constantly at 212—214°, and appeared to be a pure substance. This substance was hydrolysed by boiling with an excess of a 10 per cent. alcoholic solution of potassium hydroxide for four hours. The solvent was then removed, water added, and the resulting solid crystallised from a mixture of ethyl acetate and alcohol, from which it separated in small, colourless needles melting at 208—210° :

0·3350, dried at 115°, lost 0·0130 H_2O. $H_2O = 3{\cdot}9$.

0·1452 of anhydrous substance gave 0·4488 CO_2 and 0·1538 H_2O. $C = 84{\cdot}3$; $H = 11{\cdot}7$.

$C_{30}H_{50}O,H_2O$ requires $H_2O = 4{\cdot}0$ per cent.

$C_{30}H_{50}O$ requires $C = 84{\cdot}5$; $H = 11{\cdot}7$ per cent.

This compound is evidently a monohydric alcohol of the formula $C_{30}H_{49}\cdot OH$. As it does not agree in its properties with any substance of this formula which has hitherto been described, it is proposed to designate it *androsterol*, with reference to the specific name of the plant from which it has been obtained.

A determination of its specific rotatory power gave the following result :

0·2060, in 20 c.c. of chloroform, gave $\alpha_D + 0°37'$ in a 2-dcm. tube, whence $[\alpha]_D + 29{\cdot}9°$.

If to a solution of androsterol in acetic anhydride a few drops of concentrated sulphuric acid are added, a fine magenta-red colour slowly develops, which is permanent for several hours.

Monoacetylandrosterol, $C_{30}H_{49}O\cdot CO\cdot CH_3$.—On heating androsterol with acetic anhydride, the pure *acetyl* derivative, melting at 212—214°, was regenerated. When crystallised from ethyl acetate, it separates in long, fine needles :

0·1252 gave 0·3760 CO_2 and 0·1250 H_2O. $C = 81{\cdot}9$; $H = 11{\cdot}1$.

$C_{32}H_{52}O_2$ requires $C = 82{\cdot}0$; $H = 11{\cdot}1$ per cent.

A determination of its specific rotatory power gave the following result :

0·3025, in 20 c.c. of chloroform, gave $\alpha_D + 1°15'$ in a 2-dcm. tube, whence $[\alpha]_D + 41·3°$.

Monobromoacetylandrosterol, $C_{30}H_{48}BrO·CO·CH_3$.—One gram of acetylandrosterol was dissolved in 50 c.c. of chloroform, and to the cold solution a 5 per cent. solution of bromine in the same solvent was added, drop by drop, until a slight excess of bromine was present. The liquid, which evolved hydrogen bromide, was then at once shaken with a solution of sodium hydrogen sulphite, washed with water, dried, and the solvent removed. A syrup was thus obtained which, after treatment with ethyl acetate, yielded a crystalline product. The latter, after repeatedly crystallising from the same solvent, separated in colourless prisms, melting at 228—230°, and amounted to 0·6 gram:

0·1494 gave 0·3850 CO_2 and 0·1270 H_2O. C = 70·3; H = 9·4.
0·1570 „ 0·4026 CO_2 „ 0·1325 H_2O. C = 69·9; H = 9·3.
0·2614 „ 0·0906 AgBr. Br = 14·7.
$C_{32}H_{51}O_2Br$ requires C = 70·2; H = 9·3; Br = 14·6 per cent.

This substance is evidently a *monobromo*-derivative of acetyl androsterol.

Isolation of a New Monohydric Alcohol, Homoandrosterol, $C_{27}H_{43}·OH$.

Some of the numerous mother liquors obtained during the separation of the above-described acetyl derivative of androsterol (m. p. 212—214°) deposited on standing small amounts of sparingly soluble, prismatic needles, which, after recrystallisation from ethyl acetate, melted constantly at 234—236°. The amount of this substance was 2 grams, and its properties indicated that it was a pure compound. It was hydrolysed by boiling for four hours with an excess of a 10 per cent. alcoholic solution of potassium hydroxide, the solvent removed, water added, and the resulting solid recrystallised from dilute alcohol, from which it separated in small, colourless needles melting at 192°:

0·1201 gave 0·3702 CO_2 and 0·1270 H_2O. C = 84·0; H = 11·7.
$C_{27}H_{44}O$ requires C = 84·4; H = 11·4 per cent.

This compound is evidently a monohydric alcohol of the formula $C_{27}H_{43}·OH$. As it does not agree in its properties with any substance of this formula which has hitherto been described, and differs from androsterol by the elements C_3H_6, it is proposed to designate it *homoandrosterol*.

If to its solution in acetic anhydride a drop of concentrated sulphuric acid is added, a magenta-red colour is at once produced, which is permanent for several hours.

Monoacetylhomoandrosterol, $C_{27}H_{43}O·CO·CH_3$.—On heating homoandrosterol with acetic anhydride, the pure *acetyl* derivative, melting at 234—236°, was regenerated. It crystallises from ethyl acetate in glistening, prismatic needles:

0·1292 gave 0·3852 CO_2 and 0·1256 H_2O. C = 81·6; H = 10·8.
$C_{29}H_{46}O_2$ requires C = 81·7; H = 10·8 per cent.

A determination of its specific rotatory power gave the following result:

0·3000, in 20 c.c. of chloroform, gave α_D + 2°29′ in a 2-dcm. tube, whence $[\alpha]_D$ + 82·8°.

If to a chloroform solution of acetylhomoandrosterol bromine is added, the halogen is very slowly absorbed and hydrogen bromide is evolved. The reaction is accelerated by the addition of a little iodine. From the reaction mixture a small quantity of a *bromine* derivative was obtained, which crystallised in needles melting and decomposing at 212—214°. Owing to the limited amount of material at disposal, this derivative was not further investigated.

After the separation of the two above-described compounds, a large amount of material remained in the mother liquors, from which nothing further could be obtained in a pure state by crystallisation. It has already been mentioned that while acetylandrosterol absorbs bromine very rapidly, acetylhomoandrosterol only does so very slowly. It was, therefore, thought possible that a similar behaviour might be shown by the constituents of this mixture of acetyl derivatives, and that by taking advantage of this property some separation might be effected.

Ten grams of the mixture were therefore dissolved in 150 c.c. of chloroform, and a dilute solution of bromine in the same solvent cautiously added. It was found that 1·7 grams of the halogen were rapidly absorbed, whereas the addition of 1 molecule of bromine would have required 3·6 grams, assuming the constituents of the mixture to have the composition $C_{30}H_{49}OAc$. As soon as the rapid absorption of bromine had ceased, the excess of the halogen was removed and the solvent evaporated. A syrupy mass was thus obtained, which was dissolved in acetic acid, when, on standing, a small quantity (0·5 gram) of monobromoacetylandrosterol separated.

The material remaining in the acetic acid mother liquor was precipitated by water, and dissolved in chloroform. To this solution 5 grams of bromine were added and the mixture kept for twenty-four hours, when copious fumes of hydrogen bromide were evolved. At the end of this time the excess of bromine was removed and the solvent evaporated. A syrupy mass was thus obtained, which was dissolved in a small quantity of hot ethyl acetate, and allowed to stand for some time, when a substance separated in glistening plates. This was purified by recrystallisation from a mixture of chloroform and ether, when it formed handsome plates, melting at 266—268°, and amounted to 2 grams:

0·1425 gave 0·3681 CO_2 and 0·1210 H_2O. C = 70·4; H = 9·4.
0·1382 ,, 0·0475 AgBr. Br = 14·6.
$C_{22}H_{51}O_2Br$ requires C = 70·2; H = 9·3; Br = 14·6 per cent.

This bromine derivative differs from both of the two monobromoacetyl derivatives described above, and therefore must be derived from a substance other than androsterol or homoandrosterol. In the hope of obtaining the parent substance, attempts were made to replace the bromine by hydrogen, but these were unsuccessful.

It has already been mentioned that from the unsaponifiable material obtained from the petroleum extract of the resin (*A*) only 235 grams of crystalline products could be obtained. The remaining material (215 grams) formed a light-coloured, resinous mass, from which nothing definite could be separated, either by solvents or by fractional distillation under diminished pressure. A quantity (50 grams) of the material was acetylated, when it yielded 25 grams of a mixture of acetyl derivatives similar to that previously described.

Identification of the Fatty Acids.

The alkaline, aqueous solution of potassium salts from which the unsaponifiable material had been removed by filtration, as above described, was allowed to stand for some days, when a small quantity of a sparingly soluble potassium salt separated. This yielded an acid which melted at 72—74°, and appeared to consist chiefly of arachidic acid. The clear alkaline filtrate from which the sparingly soluble potassium salt had been removed yielded nothing on extraction with ether. It was therefore acidified and again extracted with ether, when a quantity (60 grams) of fatty acids was obtained. The latter, when distilled under diminished pressure, passed over between 240° and 260°/25 mm. as a viscid, oily liquid which solidified on cooling.

As these acids distilled within the same range of temperature as those previously obtained, which existed in the rhizome in the free state, equal parts of each portion were mixed for their examination.

A determination of the iodine value of this mixture gave the following result:

0·4807 absorbed 0·3770 iodine. Iodine value = 78·4.

Twenty grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when a portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 11 grams of liquid acids, whilst the insoluble portion gave 8 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 215° and 225°/15 mm.

A determination of the iodine value gave the following result :

0·4250 absorbed 0·6162 iodine. Iodine value = 145.

This indicated that the liquid acids consisted of a mixture of oleic acid and an acid of a higher degree of unsaturation.

In order to obtain more definite information respecting the composition of the above mixture, a quantity of it was oxidised with potassium permanganate according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes,* 1904, Vol. I, 360). This resulted in the formation of approximately equal quantities of dihydroxystearic acid (m. p. 125—127°) and tetrahydroxystearic acid (m. p. 157—160°), and, with consideration of the iodine value, it would thus appear that the liquid acids consisted of a mixture of oleic and linolic acids in about equal proportions.

The Solid Acids.—These acids were fractionally crystallised from glacial acetic acid, but no separation was effected, since all the fractions melted at about 55—62°. The analysis of these acids and of their silver salts indicated that the mixture consisted principally of palmitic and stearic acids, together with a small amount of some acid of higher carbon content.

Ether, Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin (A).

These extracts amounted to 40, 14, 11, and 30 grams respectively. The remainder of the original resin (45 grams) had undergone change and become insoluble. All the extracts were dark brown resins, and with the exception of a small quantity (7 grams) of acetovanillone and a trace of ipuranol, nothing definite could be isolated from them. The ethyl acetate extract appeared to contain some glucosidic material, as on acid hydrolysis it yielded a small quantity of sugar.

Examination of the Resin (B).

This was a dark brown powder and amounted to 110 grams. It was mixed with purified sawdust, and the mixture successively extracted in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

The ether and chloroform extracts together amounted to 7 grams, and consisted of almost pure acetovanillone.

The ethyl acetate and alcohol extracts amounted to 10 and 80 grams respectively, and consisted only of resinous material.

Examination of the Aqueous Liquid (C).

Isolation of Acetovanillone.

The aqueous liquid (*C*), which amounted to about 15 litres, was repeatedly extracted with ether, and the combined ethereal extracts, after drying over anhydrous sodium sulphate, evaporated on the water-bath to a small volume. On keeping, about 45 grams of a substance were deposited in fine prisms. This substance was collected on a filter, washed with a little ether, and recrystallised from ethyl acetate, when it separated in colourless prisms melting at 112—114°.

The ethereal filtrate and washings were united, diluted with ether to about 300 c.c., and the solution shaken with successive portions of an aqueous solution of ammonium carbonate. The alkaline liquids thus obtained yielded, on acidifying, a viscid acid liquid, from which nothing definite could be isolated.

The ethereal liquid was then shaken with successive portions of a solution of sodium carbonate. On acidifying the alkaline extracts thus obtained and extracting with ether, a further quantity (15 grams) of the above-described crystalline substance, melting at 112—114°, was obtained. This, together with the portion previously obtained, was recrystallised from ethyl acetate, when the melting point rose to 115°. The yield of pure material was about 50 grams:

0·1217 gave 0·2900 CO_2 and 0·0670 H_2O. C = 65·0; H = 6·1.

$C_9H_{10}O_3$ requires C = 65·1; H = 6·0 per cent.

A methoxyl determination by Perkin's modification of Zeisel's method gave the following result:

0·1612 gave 0·2290 AgI. OMe = 18·7.

$C_8H_7O_2 \cdot OMe$ requires OMe = 18·6 per cent.

This substance is thus seen to be acetovanillone (4-hydroxy-3-methoxyacetophenone), which was first obtained by Tiemann (*Ber.*, 1891, **24**, 2855) from another source, and has quite recently been shown by Finnemore (Trans., 1908, **93**, 1513) to be that constituent of *Apocynum cannabinum*, Linné, which had hitherto been known as "crystalline apocynin."

The identity of the above-described substance with acetovanillone was further confirmed by the preparation of its monoacetyl derivative (m. p. 57°), its methyl ether (m. p. 51°), and its phenylhydrazone (m. p. 126°) (Nietzel, *Ber.*, 1891, **24**, 2863).

The material contained in the mother liquors from which the acetovanillone had been separated, as above described, was distilled, when a further small amount of acetovanillone was obtained, together with a trace of a substance, melting at about 301°, which corresponded in its properties to dehydrodiacetovanillone (Nietzel, *Ber.*, 1891, **24**, 2688).

The aqueous liquid from which the acetovanillone had been removed by extraction with ether was treated with a solution of basic lead acetate. This produced a voluminous, yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture, a liquid was obtained which gave a bluish-black coloration with ferric chloride and evidently contained a quantity of tannin. The liquid was evaporated to dryness under diminished pressure, when about 200 grams of a brown, amorphous product were obtained, from which, however, nothing definite could be isolated.

Isolation of a Toxic, Bitter Principle, Apocynamarin, $C_{14}H_{18}O_3,H_2O$.

The filtrate from the above-mentioned basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a volume of 4·5 litres. The syrupy liquid thus obtained was kept for about four weeks, during which time a crystalline substance slowly separated. This substance was collected, washed with cold water, and dried in the air, when it amounted to 12 grams. It was purified by crystallisation from dilute alcohol, when it formed handsome, colourless prisms melting and decomposing at about 170—175°.

The air-dried substance was analysed:

0·1324 gave 0·3175 CO_2 and 0·0965 H_2O. $C = 65·4$; $H = 8·1$.

1·2010 of the air-dried substance, on drying in a vacuum, lost 0·0205 H_2O. $H_2O = 1·7$ per cent.

The substance after drying in a vacuum was analysed:

0·1390 gave 0·3390 CO_2 and 0·1020 H_2O. $C = 66·5$; $H = 8·1$.

After recrystallisation and drying in a vacuum, it was again analysed:

0·1372 gave 0·3352 CO_2 and 0·1005 H_2O. $C = 66·6$; $H = 8·1$.

0·4020 of the substance, dried in a vacuum, when heated at 110—115°, very slowly lost 0·0286 H_2O. $H_2O = 7·1$.

$C_{14}H_{18}O_3,H_2O$ requires $C = 66·7$; $H = 8·0$; $H_2O = 7·1$ per cent.

A determination of the molecular weight of the substance, dried in a vacuum, was kindly conducted by Mr. A. J. Ewins, B.Sc, according to Barger's microscopic method (Trans., 1904, **85**, 286), and gave the following result:

0·1100 in 2·41 pyridine was between 0·18 and 0·19 mol. benzil in pyridine, hence M.W. 254—240.

$C_{14}H_{20}O_4$ requires M.W. = 252.

It is evident that this substance possesses the formula $C_{14}H_{18}O_3$, and that it crystallises with one molecule of water, the small additional amount of water contained in the air-dried substance being doubtless occluded moisture. As it does not agree in its properties with any substance of the above formula which has hitherto been described, it is proposed to designate it *Apocynamarin*, with reference to the generic name of the plant from which it has been obtained, and the fact that it possesses an extremely bitter taste.

If to a solution of apocynamarin in acetic anhydride a few drops of concentrated sulphuric acid are added, a red colour is produced, which rapidly changes, first to blue and then to green, the green solution showing a fine reddish-bronze fluorescence.

On dehydrating apocynamarin by heating it at 115°, the water is only very slowly eliminated, the substance at the same time undergoing some further change, becoming brown and amorphous. The water of crystallisation may, however, be removed by prolonged boiling with chloroform, when the substance slowly dissolves. On evaporating the solvent a syrup, consisting of anhydrous apocynamarin, is obtained, and on treating this with water it at once crystallises, regenerating the original substance.

Apocynamarin is a neutral substance, but is changed by prolonged boiling with acids or alkalis. It contains no methoxyl group, and attempts to prepare an acetyl derivative resulted only in the formation of a syrup. Apocynamarin combines with phenylhydrazine, but the resulting hydrazone was amorphous and could not be obtained pure. It contained 5·6 per cent. of nitrogen, whereas theory requires 8·5 per cent. It appears, therefore, that apocynamarin contains a carbonyl group, and may be an aldehyde, since it readily reduces ammoniacal silver nitrate and alkaline potassium permanganate solutions.

Isolation of a New Glucoside, Androsin, $CH_3{\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3){\cdot}O{\cdot}C_6H_{11}O_5,2H_2O$

(*Acetovanillone Glucoside*).

The aqueous liquid from which the apocynamarin had been removed by filtration, as above described, was concentrated to the volume of 2 litres and kept for some weeks, but nothing further separated from it. The concentrated liquid, which formed a viscid syrup, contained a considerable quantity of sugar, as it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 208—210°.

One-eighth of the total liquid was diluted with water to 1 litre, and then shaken with successive portions of chloroform in order to remove any possible traces of acetovanillone. About 50 grams of concentrated sulphuric acid, diluted with an equal weight of water, were subsequently added, and the solution boiled for three hours. The contents of the flask, which consisted of a dark brown aqueous liquid and a quantity of resinous material, were allowed to cool, and then filtered. The clear, aqueous filtrate yielded on extraction with chloroform 1·5 grams of acetovanillone. It thus appears probable that the glucoside of acetovanillone was present in the original aqueous liquid and in considerable quantity, as the amount of acetovanillone liberated by hydrolysis corresponded to about 24 grams of its glucoside in the total aqueous liquid.

With the object of isolating the glucoside, 1 litre of the above-described aqueous liquid was mixed with 3 litres of alcohol, and allowed to stand for twelve hours at 0°. The clear alcoholic liquid was then decanted from the syrup which had separated, and the latter again extracted with alcohol in a similar manner. The combined alcoholic extracts were evaporated to about 2 litres, when a further quantity of syrup separated, from which the supernatant liquid was decanted. The syrup was repeatedly extracted with small quantities of absolute alcohol, and the combined alcoholic liquids were evaporated. From the resulting alcoholic extract, after a prolonged process of extraction, a quantity of a syrup was eventually obtained which was entirely soluble in ethyl acetate containing a little alcohol. This syrup was dissolved in water, and the solution repeatedly extracted with chloroform, after which it was extracted twice with cold amyl alcohol. The aqueous liquid was concentrated as far as possible under diminished pressure, the residue dried, and then extracted many times with small quantities of dry, boiling ethyl acetate. The product removed by the latter solvent was dissolved in a small quantity of alcohol, when the solution, after some days, deposited a crystalline substance. This was collected and washed with alcohol, after which it was crystallised, first from 70 per cent. alcohol and finally from water. By this means about 1 gram of a substance was obtained in long, colourless needles, melting at 218—220°:

0·2039, heated at 115°, lost 0·2100 H_2O. $H_2O = 10·4$.

$C_{15}H_{20}O_8,2H_2O$ requires $H_2O = 9·9$ per cent.

0·0980 of anhydrous substance gave 0·1969 CO_2 and 0·0560 H_2O. $C = 54·8$; $H = 6·3$.

$C_{15}H_{20}O_8$ requires $C = 54·9$; $H = 6·1$ per cent.

Half a gram of the substance was boiled for two hours with 5 per cent. aqueous sulphuric acid, when, on extracting the solution with chloroform, acetovanillone was obtained. The aqueous liquid, after being deprived of sulphuric acid and concentrated, yielded, on treatment with phenylhydrazine, *d*-phenylglucosazone, melting at 208—210°.

It is evident that the above-described substance is the glucoside of acetovanillone, and, being a new compound, it is proposed to designate it *androsin.*

Androsin is readily soluble in hot water or hot dilute alcohol, but sparingly soluble in cold water or in absolute alcohol. It is a β-glucoside, since it is hydrolysed by emulsin.

When androsin is heated with acetic anhydride, it yields an *acetyl* derivative, which crystallises from absolute alcohol in colourless needles melting at 154°.

Physiological Tests.

The physiological action of a number of the products obtained in the course of this investigation was kindly determined by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories.

The only active products obtained from resin (*A*) were the ethyl acetate and alcohol extracts, and these, when administered *per os* to dogs in doses of 0·5 gram, caused death, preceded by vomiting. The ethyl acetate and alcohol extracts of the resin (*B*) had only an emetic action. Acetovanillone, when injected intravenously into a cat, produced a small and very evanescent rise of blood pressure, whilst its glucoside, androsin, had no definite effect. One decigram of apocynamarin, when administered *per os* to a dog, had a powerful emetic action and no after effects. When, however, 10 milligrams of this substance were injected intravenously into a cat, a very large increase of blood pressure occurred, soon terminated by heart failure. Apocynamarin, when injected into the circulatory system, has also a pronounced diuretic action. The aqueous liquid from which the apocynamarin had been obtained produced some effects similar to those caused by the latter compound.

The conclusion, therefore, seems warranted that the emetic, diuretic, and cardiac tonic actions for which apocynum has been employed in therapeutics are all attributable to apocynamarin. It is probable, however, that the toxic action of the products obtained from resin (*A*) is due to another active principle. The physiological action of apocynamarin is being further investigated by Dr. H. H. Dale.

Summary.

The results of this investigation may be summarised as follows:

The material employed was the air-dried rhizome of *Apocynum androsaemifolium*, Linné. An alcoholic extract of the rhizome, when distilled with steam, yielded a small amount of an essential oil, together with some acetovanillone. The essential oil, deprived of acidic substances, distilled between 130° and 250°, and possessed a strong, persistent odour. The non-volatile constituents of the rhizome, as obtained after treating the alcoholic extract with steam, consisted of a brown resin (*A*) insoluble in either hot or cold water; a brown resin (*B*) readily soluble in the hot aqueous liquid, but which was slowly deposited on standing; and material which remained dissolved in the cold aqueous liquid. The brown resin (*A*), amounting to about 5·3 per cent. of the weight of the rhizome, yielded small quantities of ipuranol, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), and acetovanillone, palmitic, stearic, oleic, and linolic acids, and a large quantity of unsaponifiable material. From the latter, two new alcohols, *androsterol*, $C_{30}H_{49}{\cdot}OH$ (m. p. 208—210°), and *homoandrosterol*, $C_{27}H_{43}{\cdot}OH$ (m. p. 192°), were obtained, whilst the presence of a third *alcohol*, apparently isomeric with androsterol, was proved by the isolation of its *bromoacetyl* derivative (m. p. 265—268°). Androsterol yields an *acetyl* derivative (m. p. 212—214°) and a *monobromoacetyl* derivative (m. p. 228—230°). *Acetylhomoandrosterol* melts at 236°. The brown resin (*B*), amounting to 0·58 per cent. of the weight of the rhizome, yielded a further small quantity of acetovanillone. The portion of the alcohol extract of the rhizome which was soluble in cold water, and from which the above-described resins had been removed, contained large amounts of sugar and tannin. It yielded a quantity of acetovanillone (m. p. 115°), which was also present in the form of its glucoside, *androsin*, $CH_3{\cdot}CO{\cdot}C_6H_3(O{\cdot}CH_3){\cdot}O{\cdot}C_6H_{11}O_5,2H_2O$ (m. p. 218—220°), and a new substance, *apocynamarin*, $C_{14}H_{18}O_3,H_2O$ (m. p. 170—175°), which possesses an intensely bitter taste, is highly toxic, and represents the chief active constituent of the rhizome.

Addendum.

Since the above paper was written, a preliminary note by Horace Finnemore (Proc., 1909, **25**, 77) has appeared, in which he records the isolation of an active principle from the root (rhizome) of *Apocynum cannabinum*. This substance he proposes to designate "cynotoxin," and assigns to it the formula $C_{20}H_{28}O_6$. The properties attributed by Finnemore to "cynotoxin" are practically the same as those of apocynamarin, the composition of which agrees with the empirical formula $C_{14}H_{18}O_3,H_2O$. In this connexion it is significant that apocynamarin, when air-dried, yields results on analysis which are in accordance with the formula assigned by Finnemore to "cynotoxin." It has been shown, however, that air-dried apocynamarin contains, not only water of crystallisation, but also some occluded water, the latter being lost on drying in a vacuum. It therefore seems probable that the active principle of *Apocynum cannabinum* is identical with apocynamarin.

With consideration of the formula assigned by Finnemore (*loc. cit.*) to the active principle of *Apocynum cannabinum*, and his conclusion that "it is a dilactone, either of Kiliani's digitic acid, $C_{20}H_{32}O_8$ (*Ber.*, 1891, **24**, 339), or of a closely related isomeride," the present author has redetermined the molecular weight of apocynamarin.

The substance, after drying at 115° until constant in weight, gave the following result:

0·3420 in 25·00 nitrobenzene gave Δ^t $-0·192°$. M.W. = 492.

As, however, apocynamarin when dried at 115° suffers some decomposition, the molecular weight was also determined by the cryoscopic method in acetic acid solution, first with the hydrated substance, and then with anhydrous material, as obtained after removing the water of crystallisation by means of chloroform, the last traces of the latter having been expelled by anhydrous acetic acid:

0·5305 of hydrated substance in 24·65 acetic acid gave Δ^t $-0·307°$. M.W. = 268.

0·4990 of anhydrous substance in 21·50 acetic acid gave Δ^t $-0·187°$ M.W. = 473.

$C_{14}H_{18}O_3,H_2O$ requires M.W. = 252.
$C_{28}H_{36}O_6$ „ M.W. = 468.

Apocynamarin, when dehydrated by boiling with chloroform, does not appear to suffer any change other than the loss of water of crystallisation, as the material thus obtained is instantly converted into the crystalline hydrated substance when brought in contact with water. It would therefore appear probable that the values given by the anhydrous substance indicate the correct molecular weight of the compound, and that the lower figure yielded by the hydrated compound is due to the water of crystallisation.

Dr. G. Barger has kindly conducted two determinations of the molecular weight with the hydrated substance by his microscopic method, which gave the following results, and therefore support the above view.

(1) 0·0933 in 0·887 acetic acid at 80° was between 0·225 and 0·250 mol.

(2) 0·1072 in 1·914 alcohol was between 0·111 and 0·147 mol.

(1) Mean M.W. = 442. (2) Mean M.W. = 441.

The correct formula for apocynamarin would thus appear to be $C_{28}H_{36}O_6,2H_2O$, that is, double the formula assigned to it in the preceding part of this paper. The lower value obtained for the substance in pyridine solution, which indicated its formula to be $C_{14}H_{18}O_3,H_2O$, cannot as yet be explained.

The result obtained by the analysis of the phenylhydrazone of apocynamarin (p. 746) is also in agreement with the double formula, since this compound was found to contain N = 5·6, and $C_{34}H_{42}O_5N_2$ requires N = 5·0 per cent.

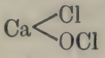
In view of the above facts it is, therefore, possible that apocynamarin is the dilactone of Kiliani's oxydigitogenic acid, $C_{28}H_{40}O_8$ (*loc. cit.*), or of an isomeride.

In conclusion, the author wishes to express his thanks to Dr. F. B. Power for suggesting this research, and for advice and assistance given throughout the course of the work.

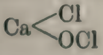
THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

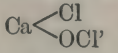
LXXXVI.—*A Crystalline Bleaching Powder.*

By KENNEDY JOSEPH PREVITÉ ORTON and WILLIAM JACOB JONES.

The constitution of bleaching powder has been a subject of controversy since Odling (1861) first suggested the graphic formula  $Ca<^{Cl}_{OCl}$ for the bleaching compound present in bleaching powder. This formula was supposed to account for the following properties of the powder: bleaching powder does not deliquesce; carbon dioxide causes the expulsion of the major part of the active chlorine (88 per cent. in most favourable circumstances). Lunge, as the result of exhaustive researches (Lunge and Schäppi, *Polyt. Journ.*, 1881, **237**, 63; compare Lunge, *Soda-Industrie*, Vol. III, p. 366, *et. seq.*), lent the great weight of his authority in favour of Odling's formula. But in reply to Kraut's criticism (*Annalen*, 1882, **214**, 354) that the non-deliquescent character of bleaching powder only indicated a "double salt" of calcium chloride and calcium hypochlorite, analogous to the non-deliquescent double salt of calcium chloride and calcium acetate,

$$CaCl_2,Ca(O_2C{\cdot}CH_3)_2,5H_2O,$$

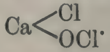
Lunge states (Lunge and Naef, *Annalen*, 1883, **219**, 130) that the formulæ  $Ca<^{Cl}_{OCl}$ and $CaCl_2,Ca(ClO)_2$ have quite the same meaning. The former merely represents the simplest composition of the bleaching compound.

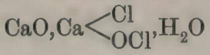
Attempts to come to a decision between these two formulæ by extracting one or other of the salts from the solid by solvents which would not decompose the compound  $\mathrm{Ca}<^{\mathrm{Cl}}_{\mathrm{OCl}}$, that is, by solvents other than water, have recently been made by von Tiesenholt (*J. pr. Chem.*, 1901, [ii], **65**, 512). He extracted the hypochlorite by a mixture of alcohol and chloroform, but inasmuch as the solvent reacts with, and does not merely dissolve one constituent, the hypochlorite, little weight can be placed on this experiment.

Light has recently been thrown on the second property of bleaching powder, the expulsion of chlorine by carbon dioxide, from several sides. von Tiesenholt (*loc. cit.*) showed that chlorine is expelled from an artificial bleaching powder, prepared by mixing calcium chloride and calcium hypochlorite, the latter being obtained by passing chlorine monoxide over dry calcium hydroxide. Later (*J. pr. Chem.*, 1906, [ii], **73**, 301), he observed that chlorine was evolved from moist mixtures of solid chlorides and hypochlorites at temperatures from 40° to 100°. These reactions indicate that hypochlorous acid (hydrolytically dissociated or expelled from its salts by carbon dioxide) attacks chlorides, yielding chlorine and the free base or the carbonate: $\mathrm{MCl} + \mathrm{HClO} = \mathrm{MOH} + \mathrm{Cl_2}$.

Moreover, the researches of Foerster (*J. pr. Chem.*, 1899, [ii], **59**, 244; *ibid.*, 1901, [ii], **63**, 141) on the mechanism of the transformation of hypochlorites, etc., into chlorates and chlorides have shown the existence of a direct action of hypochlorous acid on chlorides in which chlorine is evolved: $\mathrm{NaCl} + 6\mathrm{HClO} = \mathrm{NaClO_3} + 3\mathrm{H_2O} + 3\mathrm{Cl_2}$.

Between the decomposition of bleaching powder and the reaction studied by Foerster there is a resemblance in that the formation of chlorate accompanies the evolution of chlorine.

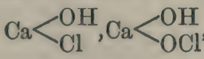
In the face of these facts the evolution of chlorine from bleaching powder under treatment with carbon dioxide can scarcely be urged as evidence of the presence of the molecule  $\mathrm{Ca}<^{\mathrm{Cl}}_{\mathrm{OCl}}$.

The constant presence of calcium hydroxide in bleaching powder has led many authorities to maintain that this substance is a necessary constituent of the compound. In recent times, Ditz (*Zeitsch. angew. Chem.*, 1901, **14**, 3, 25, 49, 105; 1902, **15**, 749) has made an elaborate study of the bleaching powder formed at different temperatures and with increasing quantities of water added to the calcium hydroxide. He infers that bleaching powder is a mixture of two compounds, compound *A*,  $\mathrm{CaO,Ca}<^{\mathrm{Cl}}_{\mathrm{OCl}}\mathrm{,H_2O}$ [which provides 30·9 per cent. active chlorine, and may be written

$$2\mathrm{Ca(OH)_2,CaCl_2,Ca(OCl)}\ ,$$

$(\mathrm{Cl{\cdot}Ca{\cdot}O{\cdot}Ca{\cdot}Cl}),(\mathrm{ClO{\cdot}Ca{\cdot}O{\cdot}Ca{\cdot}OCl}),2\mathrm{H_2O}$, or $\mathrm{Ca}{<}^{\mathrm{OH}}_{\mathrm{Cl}},\mathrm{Ca}{<}^{\mathrm{OH}}_{\mathrm{OCl}}]$, and a compound *B*, $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}},\mathrm{H_2O}$, which provides 48·9 per cent. of active chlorine. These two compounds are distinguished among other things by their behaviour when heated. Compound *A* is produced at −10°; at higher temperatures compound *B* appears. Finally, Ditz obtained a bleaching powder yielding 48·74 per cent. of active chlorine, that is, compound *B* nearly pure.

von Tiesenholt (*loc. cit.*) and Winteler (*Zeitsch. angew. Chem.*, 1902, **15**, 773), on reviewing the evidence accumulated by themselves and others, agree in the opinion that ordinary bleaching powder is a very complex material and contains basic chlorides and hypochlorites. Thus the first phase of the reaction of chlorine and calcium hydroxide would lead to the formation of a complex,



$$\mathrm{Ca}{<}^{\mathrm{OH}}_{\mathrm{Cl}},\mathrm{Ca}{<}^{\mathrm{OH}}_{\mathrm{OCl}},$$

a material of the same composition as Ditz's first compound (*A*). In highly chlorinated bleaching powders these basic salts are partly converted into normal salts. In von Tiesenholt's opinion the properties of bleaching powder, when compared with those of mixtures of chlorides and hypochlorites of metals other than calcium, necessitate the conclusion that bleaching powder contains a compound of calcium chloride and hypochlorite, either a double salt, $\mathrm{CaCl_2,Ca(ClO)_2}$ (or the basic salts), or a compound of the structure $\mathrm{Ca}{<}^{\mathrm{Cl}}_{\mathrm{OCl}}$. The formation of this complex is a property of these particular salts; it is not produced by chlorides and hypochlorites of other metals, and hence arises the peculiar suitability of calcium hydroxide (apart from its low solubility) for yielding a stable bleaching powder.

Up to the present no crystalline bleaching powder has been described, although the fact that an aqueous solution of bleaching powder yields a crystalline separation on cooling has long been known. Kingzett (Trans., 1875, **28**, 404) obtained crystals, on the one hand by cooling and, on the other, by evaporating in a vacuum over sulphuric acid a concentrated extract of the powder. His analysis of one specimen (prepared by evaporation) led to his describing them as calcium hypochlorite, $\mathrm{Ca(ClO)_2,4H_2O}$. In other preparations, however, he was not able to obtain specimens which gave very satisfactory analytical numbers.

Winteler (*loc. cit.*) states that he has frequently prepared crystals from solutions of bleaching powder by cooling in a freezing mixture. He affirms that these crystals, of which no analyses are given, are merely calcium oxychloride.

Our experiments started in the chance separation of large, prismatic crystals from a concentrated solution of bleaching powder which had been left for some weeks in a dark cupboard in the autumn. The solution could not have been exposed at any time to a lower temperature than 8°, and must have generally been at about 12°. These crystals had grown each separately from the walls of the bottle, and could thus be easily isolated from the mother liquor.

Properties.—The crystals (in all about 0·9 gram) were in the form of long (0·5 to 1·2 cm.), colourless prisms, with a lustre equal to that of lead chloride. With water they disintegrated, the solution being alkaline, and containing both chloride and hypochlorite; the residue, which was of low solubility, was mainly calcium hydroxide, but contained also both chloride and hypochlorite. The crystals behave, in fact, to water very much in the same manner as ordinary bleaching powder. This reaction with water excluded the possibility of washing the crystals with water or an aqueous salt solution (procedures which were adopted by Kingzett and Winteler).

They were kept for several weeks in an atmosphere free from carbon dioxide without material change, although their lustre gradually disappeared; the yield in active chlorine had not, however, undergone any perceptible alteration.

The crystals did not deliquesce in the air, but after several days' exposure it was found that calcium carbonate had been formed, and the hypochlorite had mostly disappeared, chloride and chlorate taking its place. The material was now deliquescent, again closely resembling bleaching powder. On heating at 100° the crystals attained constant weight after three-quarters of an hour. Although they had lost 37·5 per cent. of their weight, it was found that there was no diminution of the proportion of active chlorine.

Owing to the small quantity of material, the analyses had to be carried out on unusually small weights. Estimations were made of the water (lost at 100°), calcium, total chlorine, active chlorine, and alkalinity, that is, calcium oxide either as basic salt or as hydroxide; the latter was estimated by dissolving the crystals in excess of standard hydrochloric acid, removing the chlorine by aspiration, and then titrating the acid not neutralised. The deficiency, failing evidence of the presence of either carbonate or chlorate, was taken to be water combined as calcium hydroxide:

0·1163 set free iodine equivalent to 5·15 c.c. *N*/10 I. Active chlorine = 15·66.

0·0643 lost 0·0241 at 100°. $H_2O = 37·48$.

0·1475, after reduction with arsenite, gave 0·0942 AgCl. Cl = 15·925.

0·0960 gave 0·0389 CaO. Ca = 28·94.

0·0993 neutralised 14·17 *N*/10 HCl and 4·25 c.c. *N*/10 $Na_2S_2O_8$;
hence CaO neutralised 9·92 c.c. *N*/10 HCl. CaO = 28·0.

From these numbers: $CaCl_2$ = 12·66, $Ca(ClO)_2$ = 15·82, CaO = 28·00 H_2O = 37·48, H_2O as $Ca(OH)_2$ = 6·04 per cent.

These figures lead to a somewhat complicated formula, on the exactness of which too much stress cannot be laid, namely:
$2CaCl_2,2Ca(ClO)_2,9CaO,[5H_2O]_2,37H_2O$ or, preferably,

$$2(Cl{\cdot}Ca{\cdot}O{\cdot}Ca{\cdot}Cl),2(OCl{\cdot}Ca{\cdot}O{\cdot}Ca{\cdot}OCl),5Ca(OH)_2,37H_2O,$$

which requires: $CaCl_2$ = 12·55, $Ca(ClO)_2$ = 16·17, CaO = 28·54, H_2O = 37·65, H_2O as $Ca(OH)_2$ = 5·09 per cent.

Since calcium hydroxide has a very low solubility in water, it is obvious that no great amount of a compound with such a large proportion of calcium oxide could be obtained from a solution of bleaching powder. A comparison of the composition of the separation with that of the solution brings out a striking contrast. The bleaching powder from which the solution was prepared contained 31·16 per cent. of active chlorine; the molecular ratio $CaCl_2 : Ca(ClO)_2$ was 1·396 : 1. The solution was prepared by extracting the powder for several days with cold water, and contained $CaCl_2$ = 96·71, $Ca(ClO)_2$ = 70·15, $Ca(ClO_3)_2$ = 2·74, and $Ca(OH)_2$ = 1·7 grams per litre.* The solution contained 69·65 grams of active chlorine per litre, and its density was 1·140 at 7·7°/7·7°. The ratio $CaCl_2 : Ca(CaO)_2$ was 1·77 : 1, but the solution was far from being saturated with respect to calcium chloride.

Cooling the mother liquor to − 5° caused the separation of a small amount of white, feathery, lustrous crystals, which, owing to their form and nature, could only be very imperfectly separated from the mother liquor, and hence but approximately analysed. Both in general characters and composition they resembled the large crystals. The calcium chloride and hypochlorite were in the molecular ratio 1 : 1, but the calcium hydroxide comes out somewhat less.

Solutions of bleaching powder of other concentrations were examined. Spontaneous crystallisation at the ordinary temperature was not again observed. A very highly concentrated solution of bleaching powder ($CaCl_2$ = 141·6, $Ca(ClO)_2$ = 90·97, $Ca(OH)_2$ = 1·4 grams per litre), in which the ratio $CaCl_2 : Ca(ClO)_2$ = 2·004 : 1, yielded only at − 18° crystals simultaneously with ice. The crystals (0·7 gram separating from 1 litre of solution) resembled in all respects, except form, those described in the foregoing, the ratio $CaCl_2 : Ca(ClO)_2$

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* Lunge (*Soda-Industrie*) gives a typical composition of a solution of bleaching powder, in which he finds $Ca(OH)_2$ = 4·21 grams per litre, that is, the solution contains a quantity of calcium hydroxide which is more than twice that present in a saturated solution of the base. Moody and Leyson (Trans., 1908, **93**, 1767) find that 1 litre of water dissolves 1·643 grams of calcium hydroxide at 15°.

being still 1 : 1, in spite of the higher proportion and concentration of calcium chloride in the solution. The proportion of calcium hydroxide had still further fallen.

The description of the crystals obtained by Kingzett and Winteler leaves little doubt that the latter in any case was dealing with a similar material. He isolated it only as fine feathery needles, and records no analyses; he washed it with concentrated calcium chloride, which he states removed hypochlorite and left an insoluble material. This he took to be calcium oxychloride, and hence concluded that the original separation consisted of that substance. Moreover, he concluded that Kingzett's material was of the same nature, a conclusion which appears to have been accepted by many chemists.

The material which Kingzett obtained on cooling the solution was probably of the same nature as ours; he did not examine it minutely, but there can be no doubt that the crystals which he obtained by evaporation and analysed were of a different nature. He believed that they were a hydrated calcium hypochlorite.

To satisfy ourselves on this point, we have tried the concentration of solutions of bleaching powder: (I) by distillation under reduced pressure, and (II) by evaporation over sulphuric acid and potassium hydroxide (Kingzett's method).

When the concentration had proceeded until the solution was about $4N$ (active chlorine = 142 grams per litre), a crystalline powder began to separate. These crystals, which were characteristically soft and soapy when pressed on porous plate, are very different from the material obtained by cooling the more dilute solutions of bleaching powder. They had a strong odour of hypochlorous acid, and when warmed gave off water and chlorine. They were readily and completely soluble in water. At 100° they came to constant weight in thirty minutes, but had lost chlorine (or hypochlorous acid) besides water. Nevertheless, the percentage of active chlorine in the dry material was 71·74, whilst if the loss on heating had been only due to water, it would have been 78·8. Dehydration over sulphuric acid and potassium hydroxide was very slow, and was also accompanied by a similar loss of active chlorine. The anhydrous material was not markedly hygroscopic. Analyses were made of the hypochlorite, chloride, calcium, and alkalinity, and indicate that the substance is mainly a hydrated calcium hypochlorite ($Ca(ClO)_2 = 58{\cdot}35$, $H_2O = 28{\cdot}69$, and $Ca(OH)_2 = 9{\cdot}61$ per cent.). The ratio $Ca(ClO)_2 : H_2O$ was 1 : 4, but we find calcium hydroxide present, the ratio $Ca(OH)_2 : Ca(ClO)_2$ being 1 : 3, and hence either the substance is a basic salt or, more probably, is mixed with a basic salt.

The material is obviously identical with that described by Kingzett, and correctly believed by him to be a hydrated calcium hypochlorite, $Ca(ClO)_2,4H_2O$. Recently, the Chemische Fabrik, Griesheim-Elektron (D.R.-P. 1906, No. 188524, *Chem. Zentr.*, 1907, ii, 1950; D.R.-P. 1907, No. 195896, *Chem. Zentr.*, 1908, i, 1109) has obtained similar basic hypochlorites by evaporating solutions made by saturating milk of lime with chlorine.

Conclusions.—The most notable feature of the crystalline separations which we have obtained from bleaching powder solutions of moderate concentrations at low temperatures is the remarkable constancy of the ratio of the calcium chloride to hypochlorite.

This constancy was maintained in crystals separating from solutions in which the ratio $CaCl_2 : Ca(ClO)_2$ was not only very different, but varied; the value of the ratio was not affected by the temperature at which the separation took place. On the other hand, the proportion of calcium hydroxide and water is without doubt variable, even when full regard is had to the uncertainty of the analytical numbers. Since the yield of the crystals is obviously limited by the low solubility of the calcium hydroxide, the chloride and hypochlorite are probably in the form of basic salts.

On the other hand, from solutions which are saturated with respect to the hypochlorite, this salt, and not the compound, separates alone, at least at temperatures above 0°.

This constancy of the proportion in which the two salts are found points, in our opinion, to the existence of a compound of calcium hypochlorite and chloride, and probably also of their basic salts. This compound of the basic salts would be identical with Ditz's substance (*A*) which is obtained from calcium hydroxide at $-10°$,

$$2Ca(OH)_2,CaCl_2,Ca(OCl)_2.$$

From the variability of the calcium hydroxide in the crystals, we infer that the association of the base with the compound is of the nature of an isomorphous mixture. The alternative hypothesis, that we are dealing with a series of different basic salts, seems scarcely probable in the light of the constancy of the ratio of chloride to hypochlorite.

The nature of these crystalline compounds is entirely in harmony with, and affords strong additional evidence for, the view, which has been arrived at by a study of the properties of bleaching powder, that the powder contains a compound of calcium chloride and hypochlorite. Moreover, as recent studies of bleaching powder have shown, this compound consists of basic salts, except when the bleaching powder is exceptionally highly chlorinated. Only in the early stages of chlorination should we expect to find the calcium hydroxide playing the part which we suggest it takes in the crystalline bleaching powder.

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LXXXVII.—*The Affinity Values of Certain Alkaloids.*

By Victor Herbert Veley.

It is a matter of common knowledge that determinations of the affinity values of most naturally occurring alkaloids present considerable experimental difficulties; their insolubility in water, and in most cases the very slight hydrolysis of their salts at the ordinary temperature, preclude determinations by the electric conductivity or ester catalysis methods, and, except in a few cases, by the methyl-orange method. Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 289) gave certain results obtained by the electric conductivity method for the hydrochlorides of a few alkaloids, from which the general conclusion was arrived at that the velocity of their ions was of a comparatively low order.

On the other hand, it is well known that the greater number of alkaloids are precipitated or displaced by solutions of ammonia, although a few are not so precipitated, but only by solutions of sodium hydroxide.

To express the matter in its most general form if the functions of the affinity values of an alkaloid be represented by $\phi(b')$ and that of ammonia by $\phi(b)$, in terms of the acids, $\phi'(a)$, then in the one case $\phi'(a)\phi(b)>\phi'(a)\phi(b')$, and in the other, $\phi'(a)\phi b<\phi'(a)\phi(b')$; in any equilibrium equation $\phi'(a)$ disappears if the acid is the same in all cases. It is also known that some alkaloids will displace others from their salts, so that a classification of a general type has been arrived at.

In the present communication it is desired to give an account of results obtained (1) by the methyl-orange method in a few cases, and (2) by a precipitation method, together with a few prefatory remarks on each.

Methyl-orange Method.—Since the date of my last publications (Trans., 1908, **93**, 652, 2114, 2122; this vol., 1) Lundén (*Samml. Chem.-ü. Chem-techn. Vorträge*, 1908, **14**, 32, *et. seq.*), alluding to my method in the course of a discussion on the relative accuracy of the methods proposed for the determinations of hydrolysis and affinity values, expresses the opinion that as methyl-orange is the sodium salt of an aminosulphonic acid, some of the hydrochloric acid, whether free or liberated by the hydrolysis of a hydrochloride, is used up in the neutralisation of the amino-group to form a hydrochloride. Accepting this view, which sets forth a possible contingency, if the proportion of hydrochloric acid thus used up varies with the relative masses of acid and methyl-orange, there would be an error dependent on the mass of acid liberated by hydrolysis, but, as a matter of fact, it is found that whether the hydrolysis is 90 per cent. or 1 per cent. the results obtained by my method are concordant with those obtained by other methods against which no such objection is possible. Lundén also alludes to the possibility that the proportion of acid used up may be the cause of my result, that Arrhenius' hydrolysis formula is not applicable to the ultimate point (lim.)$x=1$, $v=\infty$, which I have attributed to a possible reversal of hydrolysis at extreme dilutions. Until some method has been devised for the accurate determination of hydrolysis values when $v<1\ 10^4$, it will not be possible to decide between the two views.

I desire to take this opportunity of replying to queries as to simple examples which are suitable for demonstrating to large classes of students the methyl-orange method as applied to illustrate differences of hydrolysis and hence of affinity values. Such examples might be (1) *o*-toluidine and benzylamine hydrochlorides, both in $N/20$ solution, as illustrating the effect of isomerism, and (2) the hydrochlorides of glycine and its ethyl ester, both in $N/20$ solution, as illustrating the effect of substitution of carboxylic hydrogen by a hydrocarbon grouping, namely, the alteration of an amphoteric electrolyte to a strongly basic substance. Both these illustrations are quite simple, and require no tintometer; 2 c.c. of the hydrochloride solutions can be added to 200 c.c. of a methyl-orange solution, which may be conveniently prepared by diluting the reagent as made up for laboratory purposes, namely, 1 : 1000, up to 1 : 100,000. The diluted solution is best when freshly prepared, but the 1 : 1000 solution appears to remain unaltered for several months.

Suitable examples for individual students, working with a tintometer,* can be selected from my papers, such as *m*-phenylenediamine hydrochloride, giving half the value of hydrochloric acid, both solutions being of same concentration; betaine or caffeine hydrochlorides, giving approximately identical values as hydrochloric acid, and others. I would only suggest the advisability of previously testing persons with coloured skeins of wool or slips of glass, as there are many, by no means colour blind, who are more or less unable to differentiate changes of tint (compare Burch, *Phil. Trans.*, 1908, *B*, **199**, 231).

Precipitation Method.—This method, described in outline in my former communication (this vol., p. 5—6), is based on the determination of the mass of sodium hydroxide contained in a hydrolysed aqueous solution of borax which is required to produce an initial precipitation of the alkaloids in aqueous solutions of their hydrochlorides; it is only applicable if the solubility of the alkaloid in water is less than 1/800, and if the hydrochloride is sufficiently soluble in water to form a $N/40$-solution at least. In detail it consists of dropping the borax solution from a burette, or in the case of smaller quantities, from a 1 c.c. pipette divided into 1/100th (both instruments being calibrated), into a known volume of alkaloid hydrochloride contained in a flask resting on black paper until a permanent precipitate is produced.

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* An improved form of instrument applicable for such work and designed according to my specifications can be obtained from Messrs. Baird and Tatlock.

The reaction, with the one exception of papaverine, was perfectly sharp. Then, as previously explained, the relative masses of sodium hydroxide contained in the borax solution, and of the alkaloid combined initially with the hydrochloric acid, form a factor of these affinities just at that point at which a homogeneous system, all substances remaining in solution, passes into a heterogeneous system, namely, precipitation of alkaloid. Hence, therefore, if $\phi(b)$ and $\phi(b)'$ be functions of the affinities of the soda and alkaloid respectively for hydrochloric acid (or of their ions for the chlorine ion), and M and M' their respective masses, then

$$\phi(b)/\phi(b') = M/M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1).$$

The same result could be arrived at by the hydrolysis equations:

$$k_b/k_w = \frac{1-x}{x^2M} \text{ and } k_b'/k_w = \frac{1-x'}{x'^2M'} \quad . \quad . \quad . \qquad (2),$$

hence

$$k_b/k_b' = x'^2(1-x)M'/x^2(1-x')M \quad . \quad . \quad . \quad . \qquad (3).$$

But as the hydrolysis both of the sodium chloride and alkaloid hydrochloride is very small, equation (3) resolves itself into equation (1) with an inappreciable error.

In order to convert the functions $\phi(b)$, $\phi(b)'$ in equation (1) into affinity values k_b, k_b' in equation (3), the following data have been utilised.

The hydrolysis of a $N/10$-sodium borate solution is taken at 1 per cent. (compare preceding communication); the relative affinities of sodium and ammonium hydroxides are, according to the mean of Ostwald's determinations by various methods, in the ratio 100 : 1·8. The affinity value of ammonia $k_{b(15)} = 1{\cdot}7\ 10^{-5}$ according to Lundén (*J. Chim. Phys.*, 1907, **3**, 574), according to Denham (Trans., 1908, **93**, 50) $k_{b(25)\ \text{calc.}} = 4\ 10^{-5}$, which corrected for temperature is $k_{b(15)} = 3{\cdot}7\ 10^{-5}$, and the mean of these two values, namely, $k_{b(13)} = 2{\cdot}7\ 10^{-5}$, has been taken. The value $k_{b(20)} = 5\ 10^{-5}$, obtained by Moore (Trans., 1907, **91**, 1382) by the chloroform extraction method, is probably too high. Hence, therefore, $M'/M \times 1{\cdot}8/100$ gives the factor (f) of the relative affinities of ammonia and an alkaloid, and also $2{\cdot}7\ 10^{-5}/f$ gives the actual affinity value of the latter.

The errors of the method depend on (i) the correctness of all the data given above; (ii) the tendency of supersaturation taking place before initial precipitation; (iii) the relative solubilities of the alkaloids, which introduces an indeterminable function, and (iv) the accuracy in reading small volumes of solutions.

As regards (iii), results obtained with $N/20$- and $N/40$-solutions of the alkaloid hydrochlorides were concordant within experimental error; as regards (ii), two to three minutes were allowed, the solutions being agitated if supersaturation was suspected. It is, of course, only desired to put forward the method as an *attempt at approximations*, since other methods are not applicable, unless an ester can be found, which is hydrolysed by a base of high affinity value within a reasonable limit of time, and is not hydrolysed by water under the same conditions. But, however this may be, it will be shown in the sequel that such approximations are in complete accordance with general conclusions which have been arrived at by physical and analytical data.

Classification of Alkaloids.

It will be proposed, for the sake of convenience only, to divide the alkaloids (including the artificially-prepared stovaine and its homologues) into three classes, as follows:

(1) Relatively weak alkaloids, the hydrochlorides of which show traces (about 1 per cent.) by the methyl-orange method at the ordinary temperature, or when their solutions are heated for a certain time (three hours) at 60°; the affinity value of these is rather less than $1\ 10^{-7}$.

(2) Stronger alkaloids, the hydrochlorides of which show no hydrolysis by the methyl-orange method under above conditions (although a few show hydrolysis when solutions are heated to 100°); the affinity value of these varies from $3\ 10^{-5}$ to $1\ 10^{-7}$ (roughly in ratio 1 : 30). It will be seen in the sequel that one or two alkaloids of affinity value less than $1\ 10^{-7}$ (and hence should belong to Class I) come in this category. Members of this class are precipitated by ammonia solution.

(3) Strongest alkaloids, not precipitated by ammonia, but precipitated by sodium hydroxide solutions, although not in all cases by a hydrolysed borax solution. The affinity value of these is greater than $3\ 10^{-5}$.

The above classification is not, of course, intended to be arbitrary.

EXPERIMENTAL.

Class I.—Narcotine.—A solution of the hydrochloride of this alkaloid was prepared by dissolving a weighed quantity of $N/20$-hydrochloric acid so as to form a $N/20$ solution of salt, presuming no hydrolysis to take place; this process required several days for completion. A few results were obtained by the methyl-orange method (series I); the solution was heated for three hours at 60° and again examined (series II), when a slight separation of alkaloid took place.

I (temp. 17°).*	II (temp. 20°).
$V=4\times10^3$.	$V=4\times10^3$.
0·4	0·75
0·7	1·4
1·0	2·1
	2·7

Value of k for I = 0·35, for II = 0·7; hydrolysis values 1·1 and 2·2; $k_{b(17)}$ from I = $7{\cdot}9\ 10^{-8}$.

Hydrastine.—The hydrochloride of this alkaloid in $N/20$-solution gave no measurable value with methyl-orange at the ordinary temperature; after heating the solution for three hours at 60° the following results were obtained:

$V=4\times10^3$ (temp. 20°).
0·6
1·1
1·6

Value of $k=0{\cdot}55$; hydrolysis value $=1{\cdot}7$. Hence hydrastine is a stronger base than narcotine; its affinity value is probably about $1\ 10^{-7}$.

Papaverine.—The behaviour of a $N/20$-solution of the hydrochloride of this alkaloid was precisely similar to that of hydrastine solution; after heating for three hours at 60° the following results were obtained:

$V=4\times10^3$ (temp. 20°).
0·6
1·2
1·7

Value of $k=0{\cdot}6$; hydrolysis value $=1{\cdot}9$. Papaverine is therefore intermediate between hydrastine and narcotine, and its affinity value $k_b=9\ 10^{-8}$ approximately.

The sodium borate precipitation method was not available in the case of papaverine, as the reaction was not sharp; the precipitate at first formed slowly dissolved, the rapidity of the re-solution decreasing with increase of borate solution added.

On comparison of the two allied alkaloids, narcotine and papaverine, it is evident from the above that the order is papaverine > narcotine; this result is in complete accordance with the thermochemical investigations of Leroy (*Compt. rend.*, 1899, **129**, 220), who obtained values

Papaverine + 1 mol. HCl	$\phi=41{\cdot}5$
Narcotine + ,, HCl	$\phi=23{\cdot}3$

although both numbers are lower than might be expected.

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* The methods of stating results and factors are those adopted in my previous communications.

As both papaverine and narcotine consist of conjoint benzyl and *iso*quinoline residues (Freund and Becker, *Ber.*, 1903, 36, 152: narcotine. Goldschmidt, *Monatsh*, 1884, 7, 495; Pope and Peachey, Trans., 1898, 73, 893: papaverine), it is clear that the high affinity value of benzylamine, $k_b = 2{\cdot}4\ 10^{-5}$, is modified by that of the *iso*quinoline, $k_b = 3{\cdot}6\ 10^{-10}$, the nitrogen atom being common to both, the affinity values, $k_b = 8$ to $9\ 10^{-8}$, of the alkaloid not being widely removed from the mean of the values of the two component bases. Their case is precisely analogous to that of tropine (compare former communication).

Narceine.—The hydrochloride was not sufficiently soluble in water for the purpose of this investigation.

Class II.—Of the alkaloids of this class, only cocaine hydrochloride showed any measurable trace of hydrolysis by the methyl-orange method when the solution was heated for three hours at 100°. This alkaloid was dealt with in my previous communication as a derivative of tropine; it is only desired to alter the value of k_b from 2·5 to $4\ 10^{-7}$ on account of alteration of ammonia factor.

Aconitine.—The affinity value of this alkaloid was found to be about $3\ 10^{-8}$ by the borax precipitation method; it would therefore be expected that its hydrochloride would be sufficiently hydrolysed to give a reaction by the methyl-orange method, but none could be detected even after prolonged heating of the solution at 60°. In any case the comparatively high affinity value is remarkable, having regard to the presence of the acidic groupings, namely, benzoyl and acetyl, as shown by Dunstan (Trans., 1894, 65, 292); but until the constitution of the aconine residue becomes a matter of more accurate knowledge the above result cannot be duly interpreted.

Stovaine and its Homologues.—These compounds, although not strictly alkaloids, can be considered under this class. The values obtained by the borax precipitation method for (1) stovaine or (dimethylaminomethyl)methylethylcarbinol benzoate hydrochloride, $OBz{\cdot}CMeEt{\cdot}CH_2{\cdot}NMe_2,HCl$, and (2) the corresponding methyl derivative, $OBz{\cdot}CMe_2{\cdot}CH_2{\cdot}NMe_2,HCl$, are given in the following table, in which M' = mass of base, dissolved as hydrochloride, in decimilligrams, M = mass of sodium hydroxide contained in the volume of borax solution required to produce precipitation, f the factor in terms of ammonia, namely, $M'/M \times 1{\cdot}8/100$ (compare *supra*), and k_b the derived affinity value at temperature, approximately 15°. (The figures given in succeeding tables will have the same significance.)

	M.	M.	f.	$k_b\ 10^{-7}$.
(I.)	1185	0·12	179	1·51
(II.)	1115	0·24	84	3·22

The corresponding *iso*amyl and phenyl derivatives gave precipitates with the borax solution so immediately that accurate results could not be obtained; their affinity values are, therefore, about 1 10^{-7}.

Two points appear to be of interest, (i) that the dimethyl derivative is a stronger base than the methylethyl derivative, and both are stronger than the *iso*amyl and phenyl derivatives, and (ii) the relatively high affinity value of all the bases having regard to the presence of the benzoyl grouping, thus presenting cases analogous to that of aconitine, which they further resemble in that their solutions, after heating for some hours at 100°, show no hydrolysis measurable by the methyl-orange method.

The results obtained for stovaine illustrate in a quantitative manner the necessity, insisted upon in writings * on anæsthetics for washing out syringes, previously used for borax solutions, before introducing stovaine solutions.

The Cinchona Alkaloids.—In my former communication it was pointed out that the affinity value of the stronger or piperidine residue was less than that of ammonia and greater than 1 10^{-7} (Trans., 1908, **93**, 2116); on applying the borax precipitation method, this conclusion was confirmed.

In two cases experiments were conducted with $N/20$- and $N/40$-solutions of the hydrochlorides, and the results obtained were within the limits of experimental error. In the following table the details are given:

	M'.	M.	f.	$k_b\ 10^{-7}$.
Quinine	1524	0·24	125 (mean)	2·16
,, ...	762	0·14		
Quinidine	762	0·12	114	2·36
Cinchonine	1471	0·16	165·5	1·63
Cinchonidine ...	1471	0·28	91·5 (mean)	3·72
,, ...	735·5	0·15		

The only point in the above figures which calls for comment is the low value obtained for cinchonine, as it would be expected from thermochemical determinations that the order would be cinchonine = cinchonidine > quinine = quinidine, which is that found with the exception of the first named.

But, however this may be, the cinchona alkaloids, as a class, present cases analogous to that of tropine, in that the high affinity value of the piperidine nucleus is modified by being conjoined to the weaker quinoline nucleus.

Strychnine.—The following values were obtained with a $N/20$-solution of the hydrochloride:

M'.	M.	f.	$k_b\ 10^{-7}$.
1670	0·16	189	1·43

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* The references in clinical journals published in this country, France, and Germany are too numerous to give in detail.

In this case, also, the affinity value of the stronger hydropyridine nucleus is modified by being conjoined to another grouping, probably that of *iso*quinoline, the nitrogen atom of which forms part of an acidic residue (compare Trans., 1908, **93**, 2120).

Gelsemine.—A *N*/40-solution of the hydrochloride was used, owing to the sparing solubility of the salt; the values obtained are as under:

M'.	*M*.	*f*.	$k_b\ 10^{-6}$.
2230	2·64	15·2	1·8

Emetine.—I am indebted to Mr. W. C. Reynolds for a sample of the hydrobromide ($C_{15}H_{22}O_{11}N,HBr,2H_2O$) of this alkaloid, which is the salt most conveniently obtained, the free base, as also its solution in hydrochloric acid, turning a yellow colour quickly owing to absorption of oxygen from the air. The following values were obtained with a *N*/20-solution of the salt, three quite concordant determinations being made:

M'.	*M*.	*f*.	$k_b\ 10^{-5}$.
2380	33·6	1·22	1·98

The above result may not, of course, be quite strictly comparable with the others given, as the hydrobromide, instead of the hydrochloride, was used.

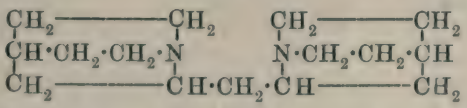
Class III.—Alkaloids of affinity value greater than ammonia.

Brucine.—The following values were obtained:

M'.	*M*.	*f*.	$k_b\ 10^{-4}$.
1672	80	0·376	7·2

Attention was called in my previous communication to the great difference between the affinity values of brucine and its congener, strychnine.

Sparteine.—No precipitation or turbidity was produced by the *N*/10-borax solution; hence its affinity value is greater than about 1 10^{-4}. This result is in accordance with the most recent views of Moureu and Valeur (*Compt. rend.*, 1903, **141**, 261 and 328), who regard this alkaloid as a dipiperidyl derivative of constitutional formula:



As both the residues are alike, there would be no modification, the one of the other, hence the affinity of both would be approximately that of piperidine, 1 10^{-3}.

Cotarnine.—Experiments with the hydrochloride of this alkaloid by the borax precipitation method led to a negative result; it would appear that under such conditions the salt would be converted mainly into the ammonium base form, and into a small proportion only of the carbinol form (Dobbie, Lander, and Tinkler, Trans., 1903, **83**, 605; compare Hantzsch and Kalb, *Ber.*, 1899, **32**, 3109).

But, however this may be, it is evident that cotarnine should be placed among the alkaloids of high affinity value, a conclusion which is confirmed by the observations of Dobbie and his co-workers as to the difference of the amount of change produced on the hydrochloride by ammonia as compared with the alkaline and alkaline earth hydroxides.

The affinity values k_b (about 15°), as determined by the methods adopted, of the naturally occurring alkaloids are put together in the following table (that of ammonia being introduced for the sake of comparison); in column N_1 the values in ascending order are given for mono-nitrogen bases, and those of the stronger grouping of the di-nitrogen bases; in column N_2, the values of the weaker grouping of the latter. The wide difference between the N_1 and N_2 values is very remarkable, and illustrates the difficulty of obtaining salts of the general type B,2HCl.

Name.	N_1.	N_2.
Aconitine	3 10^{-8}	—
Narcotine	7·9 10^{-8}	—
Papaverine	ca 9 10^{-8}	—
Hydrastine	ca 1 10^{-7}	—
Pilocarpine	ca 1 10^{-7}	4·2 10^{-11}
Strychnine	1·42 10^{-7}	6 10^{-11}
Cinchonine	1·63 10^{-7}	3·32 10^{-10}
Quinine	2·16 10^{-7}	3·32 10^{-10}
Quinidine	2·36 10^{-7}	3·19 10^{-10}
Cinchonidine	3·72 10^{-7}	3·32 10^{-10}
Cocaine	4 10^{-7}	—
Gelsemine	1·8 10^{-7}	nil
Emetine	1·98 10^{-5}	—
Ammonia	2·7 10^{-5}	—
Brucine	7·2 10^{-4}	2·52 10^{-11}
Sparteine Cotarnine	>10 10^{-4}	—

Summary.

(i) Determinations are given of the affinity values of some of the important alkaloids by the methyl-orange method, as described in former communications and the borax precipitation method, only put forward as giving approximate results for cases in which the insolubility and high affinity value preclude the application of the electric conductivity and ester catalysis methods.

(ii) It is shown that the affinity values of only a few alkaloids, mainly those derived from opium, are less than 1 10^{-7}, those of the greater number are between the limits of 1 10^{-7} and 3 10^{-5} (value of ammonia), and lastly, only a few have a value higher than the last figure, and hence may be classed with the tetra-alkylammonium hydroxides. Possibly some further information as to the last class might be obtained by a study of the relative absorptive power of carbon dioxide.

(iii) It appears in most cases that when alkaloids consist of two conjoint residues, which, if considered each by itself, would give affinity values of a widely different order, such as piperidine or benzylamine, on the one hand, and quinoline or pyrrolidine, on the other, the stronger residue is modified by the presence of the weaker. It seems to be immaterial whether each residue contains a nitrogen atom (case of cinchona alkaloids) or whether a nitrogen atom is common to both (cases of tropine, papaverine, narcotine, etc.).

(iv) The affinity values of certain mono- and di-nitrogen alkaloids, as determined by the methods applied, are collected together in a table for the sake of comparison.

I have again to express my obligations to the Research Fund Committee of the Chemical Society for a grant for purchase of materials, and also to Messrs. Burroughs Wellcome & Co., for kindly supplying me with certain samples of alkaloids and their salts for the purpose of this investigation.

LXXXVIII.—*Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules.*

By Norman Leslie Gebhard and Herbert Bryan Thompson.

The action of β-arylhydroxylamines on diazonium salts has formed the subject of several papers (compare Bamberger, *Ber.*, 1896, **29**, 103; 1897, **30**, 2280). When such a hydroxylamine (or a β-alkylhydroxylamine, *Ber.*, 1897, **30**, 2282) reacts with a diazonium salt under favourable conditions, a reaction takes place according to the following equation:

$$Ar\cdot NH\cdot OH + ClN_2\cdot R = Ar\cdot N(OH)\cdot N\colon N\cdot R + HCl,$$

and a diazohydroxylamino-compound is formed (for other literature on this subject compare Walther, *J. pr. Chem.*, 1895, [ii], **52**, 144; Barr, *Ber.*, 1887, **20**, 1497; O. Fischer and Wacker, *Ber.*, 1888, **21**, 2609; 1889, **22**, 622; Bamberger and Landsteiner, *Ber.*, 1893, **26**, 483). These diazohydroxylamino-compounds differ in several respects from the closely related diazoamines, chiefly in their behaviour towards reagents, for whilst the compound formed by the interaction of an amine and a diazonium salt reacts as if it existed in two tautomeric forms, a similar phenomenon is not shown by the substance resulting from a hydroxylamine and a diazonium salt; thus the two forms:

$$R\cdot NH\cdot N\colon N\cdot R_1 \text{ and } R\cdot N\colon N\cdot NH\cdot R_1$$

are identical, and the imino-hydrogen atom is looked upon as being "mobile" (Meldola and Streatfeild, Trans., 1887, **51**, 102, 434; 1888, **53**, 664; 1889, **55**, 412; 1890, **57**, 785). On the other hand, the two forms:

$$R\cdot N(OH)\cdot N\colon N\cdot R_1 \text{ and } R\cdot N\colon N\cdot N(OH)\cdot R_1$$

are quite distinct (Bamberger, *Ber.*, 1896, **29**, 104).

Only a limited number of these diazohydroxylamino-compounds have been described, so that the preparation of a further number was of interest; at the same time the object of the research was widened considerably by the attempt to select such compounds as might lead to the determination of the influence of the various substituting groups on the general stability of the molecule.

Two methods are possible for carrying out this idea:

(1) By using the same β-arylhydroxylamine throughout all the experiments and acting on it with differently substituted diazonium salts, and

(2) By using the same diazonium salt throughout and acting on it with differently substituted β-arylhydroxylamines.

The former method has been adopted in the present paper, which deals only with those diazohydroxylamino-compounds resulting from the action of differently substituted diazonium salts on the same β-arylhydroxylamine (compare Bamberger and Rising, *Annalen*, 1901, **316**, 257). The hydroxylamine chosen as typical of its class was *p*-tolylhydroxylamine (compare D'Orsa, *Diss. Wiesbaden*, 1896), chiefly by reason of its ease of preparation.

The parent substance to be considered is benzenediazohydroxylamino-*p*-toluene,

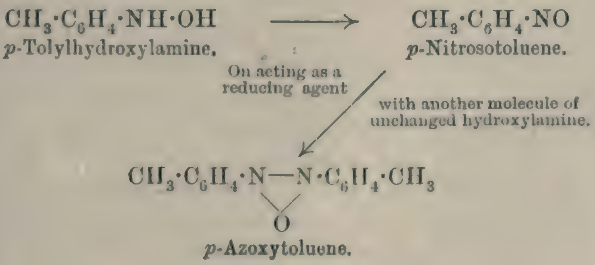
$$C_6H_5\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me,$$

obtained by the action of *p*-tolylhydroxylamine on benzenediazonium chloride; all the other substances described may be regarded as substitution products of this. Only mono-substituted derivatives have been considered, and those substituting groups only chosen which are commonly met with, namely: methyl, nitro-, bromo-, hydroxyl, sulphonic acid, and carbethoxyl groups.

Primarily, only the ortho-substituted compounds were prepared, and attempts were made to determine the influence of the substituting group on the power of reactivity of the diazonium salt from considerations of the various yields obtained (Bamberger and Rising *loc. cit.*); this method was found to be untrustworthy; first, because of the immense difficulty in keeping the conditions of the experiment identical for all combinations, and secondly, because of the presence (due to secondary reactions) of substances other than the diazohydroxylamino-compounds, which might or might not influence the velocity of the various reactions. For these reasons, then, the procedure of Bamberger and Rising (*loc. cit.*) was not adopted. The best method of preparation for each individual diazohydroxylamino-compound was worked out, and the substances were obtained in the pure state in as good a yield as possible. The real influence of the substituting groups was then determined from experiments on the decomposition of the pure substances by specified means, and not from observations of the rate of formation of the compound in question. In this way the influence (if any) of any by-products formed during their preparation was entirely eliminated. The scope of the work was further increased by the inclusion of the other isomerides containing substituting groups in the para- and meta-positions respectively. The results of work on the decomposition of the various compounds described in this paper will form the subject of a future communication.

Preparation of the Diazohydroxylamino-compounds.

The method made use of in each case consisted in the addition of a solution of *p*-tolylhydroxylamine in 90 per cent. alcohol, and cooled to about $-5°$ to a similarly cooled solution of the diazonium salt in water, the proportions of the reacting substances being those demanded by their equation of formation. The concentration in each case was kept as near as possible the same. Considerable difficulty was initially experienced in preventing the reaction from proceeding in other than the desired direction, the two most important factors affecting this being temperature and concentration. Increase of temperature and diminution of concentration both appeared to increase the reducing properties of the hydroxylamine, which generally caused nitrogen to be evolved and *p*-azoxytoluene to be formed. This decomposition may be formulated thus:



$CH_3 \cdot C_6H_4 \cdot NH \cdot OH \longrightarrow CH_3 \cdot C_6H_4 \cdot NO$

$CH_3 \cdot C_6H_4 \cdot N - N \cdot C_6H_4 \cdot CH_3$ (with O bridging the two N atoms)

p-Tolylhydroxylamine.
p-Nitrosotoluene.
On acting as a reducing agent
with another molecule of unchanged hydroxylamine.
p-Azoxytoluene.

The experiments on the effect of temperature and concentration were carried out initially in the preparation of *o*-carbethoxybenzenediazohydroxylamino-*p*-toluene, and from the results obtained it was found possible to prepare all the subsequent substances quite easily and without the formation of by-products in any quantity.

Attempts to prepare hydroxy- and sulphonic acid derivatives were not attended by success. In the case of the phenols, all efforts to effect a direct coupling failed, a large amount of *p*-azoxytoluene only resulting (compare the experience of A. Wohl, *Ber.*, 1903, **36**, 4143, on the production of similarly substituted diazoamino-compounds, who accounts for their non-formation on theoretical grounds). Regarding the sulphonic acid derivatives, many direct coupling experiments were tried, but owing to the poorness of the yields and the extreme difficulty found in purifying the products, further work in this direction was abandoned.

General Properties of the Diazohydroxylamino-compounds.

All the compounds prepared by us are finely crystalline solids, showing a tendency to become darker in colour on exposure to light, a fact particularly noticeable in the case of the more unstable ones: the unsubstituted benzenediazohydroxylamino-*p*-toluene and its methyl substituted derivatives coming first in this category, whilst the more stable ones, the nitro-derivatives, for example, can be exposed to light and the atmosphere for an indefinite period without any deep-seated change taking place. Almost all are of a faint yellow colour, which is intensified only on the entrance of a chromogenic group, for instance, the nitro-group into their molecule, and here is to be observed, too, the fact that, of the three different nitro-substitution products prepared, the ortho-derivative is the most highly coloured, which is evidently occasioned by the closer proximity of the nitro- and azo-groups or the two chromogenic groups to one another in the ortho- than in the meta- and para-isomerides. The melting points should be better termed temperatures of decomposition, being always attended by frothing and gas evolution. Great care is necessary in the selection of solvents for the initial purification of these substances, as, when they are in the impure state, they are particularly easily decomposed; in some cases the mere boiling of the impure substance with acetone or chloroform, or gentle warming with methyl alcohol, was sufficient to bring about a violent gas evolution; on the other hand, when once in the pure state they may be crystallised from almost any solvent with impunity. Generally speaking, acids have a decomposing influence (Bamberger, *Ber.*, 1897, **30**, 2284). The action of hot or cold aqueous hydrochloric acid, dilute and concentrated, is a moderately mild one; when applied in an organic solvent, however, its action is far more powerful. Alkali hydroxides possess a slight solvent action, a faintly yellow solution generally resulting, evidently attributable to salt formation owing to the presence of a hydroxyl group in the molecule. If the compound be initially dissolved in alcohol, the yellow coloration becomes more distinct on addition of alkali, and the yellow colour varies in depth with the substituting group contained in the molecule. The acidic nature of the hydroxyl group is further shown by the action of bases, like ammonia, methylamine, etc., which, when applied in absolute alcoholic solution in the cold, gradually deposit crystals of the salts; weaker bases, like aniline, do not give this reaction. It is further found that the reducing action of the hydroxylamine has not entirely disappeared, for when treated in alcoholic solution with cold ammoniacal silver nitrate, a yellow precipitate at first results (evidently due to salt formation), which gradually becomes darker and darker on slight warming, and a silver mirror is deposited, a gas evolution taking place, and an odour like that of a nitroso-compound becoming evident. Whether any reduction takes place with Fehling's solution is extremely doubtful. One of the most characteristic reactions which these compounds show is that in alcoholic solution towards ferric chloride, when a coloration varying from a deep bluish-black to a bright grass-green is obtained (compare Bamberger, *Ber.*, 1897, **30**, 2280); whilst in glacial acetic acid solution other colorations are almost invariably given with the two naphthylamines respectively.

EXPERIMENTAL.

p-Tolylhydroxylamine was prepared according to the directions of D'Orsa (*Diss. Wiesbaden*, 1896). On account of its tendency to decompose, it was found necessary in all the experiments to prepare the compound immediately before use, otherwise it became so impure that it was practically insoluble in alcohol, and the yield of the condensation product prepared from it was very poor.

The following general method of preparation of the diazohydroxylamino-compounds was uniformly adopted. The amine, dissolved in water and hydrochloric acid, was diazotised at about −10°, and to it was slowly added with constant shaking a well-cooled solution of the calculated amount of *p*-tolylhydroxylamine in alcohol and hydrochloric acid. The product of the reaction was immediately precipitated, and, after diluting with ice-water and keeping in the freezing mixture for a couple of hours, the liquid was filtered, the resulting solid dried on a porous plate, and recrystallised from suitable media until of constant melting point.

Benzenediazohydroxylamino-*p*-toluene crystallises in short, flat needles, melting and decomposing at 125·5—126° (Bamberger, *Ber.*, 1900, **33**, 3508, gives 123·5—124°). It is sparingly soluble in alcohol or light petroleum, but very readily so in benzene, ether, acetone or chloroform.

The substance is decomposed by warming with concentrated hydrochloric acid. A yellow turbidity is produced by adding ammoniacal silver nitrate to the alcoholic solution, gentle warming causing the deposition of a silver mirror. Ferric chloride gives an intense greenish-black coloration.

The glacial acetic acid solution gives with α-naphthylamine a faint pink, and with β-naphthylamine a yellow, coloration, both of which become deeper on warming and eventually turbid. The substance is readily soluble in cold concentrated sulphuric acid to a deep yellow solution, which turns intense green on gentle warming.

o-*Tolyldiazohydroxylamino*-p-*toluene*, $C_6H_4Me\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me$, crystallises in pale yellow, columnar, glassy prisms with domed ends, and melts at 103·5°. The compound is rather unstable, particularly when in an impure state. It is sparingly soluble in cold methyl alcohol and light petroleum, more readily so in ethyl alcohol or ethyl acetate, and easily so in ether, chloroform or benzene; on warming, however, it dissolves very readily in all these solvents:

0·1750 gave 0·4480 CO_2 and 0·1040 H_2O. C = 69·81; H = 6·60.
0·1458 „ 22·3 c.c. N_2 at 20·5° and 764 mm. N = 17·54.
$C_{14}H_{15}ON_3$ requires C = 69·72; H = 6·22; N = 17·43 per cent.

On warming the substance with 2*N*-sodium hydroxide, the solution turns yellow and a gas is evolved. The addition of ammoniacal silver nitrate to an alcoholic solution of the substance occasions a yellow precipitate, which rapidly darkens on warming, gas being evolved and a silver mirror deposited. Ferric chloride gives a deep bluish-black coloration, which assumes a green tinge on heating. α-Naphthylamine gives a yellow coloration, turning a deep reddish-brown on warming; with β-naphthylamine the colour changes from very faint magenta to red. The substance is soluble in cold concentrated sulphuric acid to a deep green solution, and its glacial acetic acid solution decomposes on warming.

m-*Tolyldiazohydroxylamino*-p-*toluene*, $C_6H_4Me\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me$, crystallises in long, slender, yellow prisms, the domes at the ends of which are sharply defined; it melts at 136·5°.

It is sparingly soluble in hot or cold ether or light petroleum, more readily so in alcohol, benzene or acetone, and very readily so in chloroform:

0·1691 gave 0·4342 CO_2 and 0·0959 H_2O. C = 70·01; H = 6·30.
0·1351 „ 20·3 c.c. N_2 at 18° and 756 mm. N = 17·26.
$C_{14}H_{15}ON_3$ requires C = 69·72; H = 6·22; N = 17·43 per cent.

The substance is readily decomposed on warming with hydrochloric acid, both concentrated and dilute. Ammoniacal silver nitrate is rapidly reduced, a fine silver mirror being deposited.

Ferric chloride produces a beautiful bluish-black coloration.

α-Naphthylamine causes a magenta, and β-naphthylamine a yellow, coloration. Cold concentrated sulphuric acid dissolves the substance, forming a fine green solution, which turns brown on warming.

p-*Tolyldiazohydroxylamino*-p-*toluene*, $C_6H_4Me\cdot N{:}N\cdot N(OH)\cdot C_6H_4Me$, crystallises in long, slender, canary-yellow prisms, melting at 130·5°. It is sparingly soluble in light petroleum, alcohol, glacial acetic acid or ether, dissolving more readily in acetone or chloroform :

0·1950 gave 0·4960 CO_2 and 0·1136 H_2O. C = 69·44 ; H = 6·47.
0·1320 „ 19·6 c.c. N_2 at 16° and 757 mm. N = 17·26.
$C_{14}H_{15}ON_3$ requires C = 69·72 ; H = 6·22 ; N = 17·43 per cent.

The substance is rapidly decomposed by warming with hydrochloric acid. Ammoniacal silver nitrate is reduced with deposition of a silver mirror. Ferric chloride gives a greenish-blue-black coloration ; α- and β-naphthylamines produce magenta and deep yellow colorations respectively.

o-*Carbethoxybenzenediazohydroxylamino*-p-*toluene*,

$$CO_2Et\cdot C_6H_4\cdot N{:}N\cdot N(OH)\cdot C_6H_4Me.$$

—This compound was the first of the series prepared in the course of the present investigation, and many experiments were carried out with the view of ascertaining the most suitable conditions of temperature and concentration. The former is apparently a most important factor, since, at a temperature of about 10°, the hydroxylamine exerts a reducing action on the diazo-compound, and is thereby oxidised to *p*-azoxytoluene, very little, if any, of the diazohydroxylamino-compound being formed.

On carrying out the experiment, however, at −5°, the diazohydroxylamino-compound was obtained in long, slender, pale yellow prisms melting at 122·5°. It is sparingly soluble in cold light petroleum or alcohol, more readily so in ether, and very easily so in benzene, chloroform or acetone :

0·1362 gave 0·3178 CO_2 and 0·0720 H_2O. C = 64·31 ; H = 5·87
0·1764 „ 21·3 c.c. N_2 at 13° and 748 mm. N = 14·02.
$C_{16}H_{17}O_3N_3$ requires C = 64·21 ; H = 5·69 ; N = 14·05 per cent.

Hydrochloric acid is apparently without action on the substance, and ammoniacal silver nitrate is only reduced to a very slight extent even on boiling. Ferric chloride gives a dark greenish-blue coloration, whilst α-naphthylamine produces a pink, and β-naphthylamine a red, colour. Concentrated sulphuric acid dissolves the substance in the cold to a deep yellow solution.

m-*Carbethoxybenzenediazohydroxylamino*-p-*toluene*,

$CO_2Et\cdot C_6H_4\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me$.

—This compound is almost identical in appearance with the corresponding ortho-derivative, and melts at 149—150°. It is sparingly soluble in all the common organic solvents with the exception of chloroform; on warming, it dissolves readily in glacial acetic acid, benzene or alcohol:

0·1395 gave 0·3289 CO_2 and 0·0711 H_2O. C = 64·30; H = 5·66.
0·1239 „ 15·7 c.c. N_2 at 21° and 756 mm. N = 14·35.
$C_{16}H_{17}O_3N_3$ requires C = 64·21; H = 5·69; N = 14·05 per cent.

—The substance is decomposed by warming with dilute hydrochloric acid, and ammoniacal silver nitrate suffers reduction in the cold, a faint silver mirror being formed on warming. Ferric chloride produces a fine blue coloration, and α- and β-naphthylamines give pink and yellow ones respectively. The substance undergoes decomposition on warming with alkalis.

p-*Carbethoxybenzenediazohydroxylamino*-p-*toluene*,

$CO_2Et\cdot C_6H_4\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me$.

—This compound crystallises in canary-yellow, long, slender, hair-like needles with glistening, silky lustre, and melts at 144—145°. It is very sparingly soluble in light petroleum, more readily so in alcohol or ether, and very easily so in chloroform, benzene or ethyl acetate:

0·1494 gave 0·3497 CO_2 and 0·0771 H_2O. C = 63·83; H = 5·73.
0·1543 „ 19·8 c.c. N_2 at 25° and 767 mm. N = 14·45.
$C_{16}H_{17}O_3N_3$ requires C = 64·21; H = 5·69; N = 14·05 per cent.

—Hydrochloric acid is without action on the substance, and ammoniacal silver nitrate shows only a trace of reduction even on boiling. Ferric chloride gives a blackish-green precipitate, and α-naphthylamine produces a pink, and β-naphthylamine a yellow, coloration. The substance is readily soluble in cold concentrated sulphuric acid.

o-*Nitrobenzenediazohydroxylamino*-p-*toluene*,

$NO_2\cdot C_6H_4\cdot N\colon N\cdot N(OH)\cdot C_6H_4Me$,

was obtained as a brilliant, golden-orange-coloured substance, crystallising in fine, apparently monoclinic, plates melting at 173—173·5°. It is very sparingly soluble in ether or light petroleum, more readily so in alcohol, acetone, benzene or glacial acetic acid, and dissolves easily in chloroform:

0·1583 gave 0·3319 CO_2 and 0·0659 H_2O. C = 57·19; H = 4·62.
0·1320 „ 23·2 c.c. N_2 at 11° and 743 mm. N = 20·48.
$C_{13}H_{12}O_3N_4$ requires C = 57·34; H = 4·41; N = 20·58 per cent.

The substance is unacted on by hydrochloric acid, but ammoniacal silver nitrate suffers reduction slowly on heating. Ferric chloride produces a greenish-yellow coloration, turning brown on warming, The naphthylamines give no colour reaction in the cold, but, on warming, a very deep red is produced in both cases. On warming with alkalis, a deep red coloration is obtained, which on the addition of alcohol becomes a very deep crimson. The sulphuric acid solution possesses a deep red colour.

m-*Nitrobenzenediazohydroxylamino*-p-*toluene*,

$$NO_2 \cdot C_6H_4 \cdot N{:}N \cdot N(OH) \cdot C_6H_4Me,$$

crystallises in long, slender, sharply pointed, bright yellow needles melting at 184°, much resembling masses of thorns in their manner of grouping.

In the cold it is very sparingly soluble in the common organic solvents; on warming, however, it dissolves rather more readily in glacial acetic acid, benzene, toluene or chloroform:

0·1377 gave 0·2880 CO_2 and 0·0589 H_2O. C = 57·03; H = 4·75.
0·0925 „ 16·4 c.c. N_2 at 21° and 763 mm. N = 20·28.
$C_{13}H_{12}O_3N_4$ requires C = 57·34; H = 4·41; N = 20·58 per cent.

The substance suffers slight decomposition on heating with concentrated hydrochloric acid. It is questionable whether ammoniacal silver nitrate undergoes reduction, the yellow precipitate initially formed gradually turning brown on prolonged boiling. Ferric chloride gives a dark green coloration, which assumes a violet tinge on warming. The naphthylamines produce no coloration in the cold; on warming, a reddish-brown colour is developed in both cases.

p-*Nitrobenzenediazohydroxylamino*-p-*toluene*,

$$NO_2 \cdot C_6H_4 \cdot N{:}N \cdot N(OH) \cdot C_6H_4Me,$$

crystallises in long, sharply pointed, bright yellow needles and melts at 188°, the melting-point being, however, rather dependent on the rate of heating. It is very sparingly soluble in the cold in the usual organic solvents, but dissolves fairly readily on warming in chloroform, glacial acetic acid or benzene:

0·1567 gave 0·3282 CO_2 and 0·0625 H_2O. C = 57·13; H = 4·43.
0·0954 „ 17·1 c.c. N_2 at 22° and 766 mm. N = 20·48.
$C_{13}H_{12}O_3N_4$ requires C = 57·34; H = 4·41; N = 20·58 per cent.

Hydrochloric acid has no action on the substance, and ammoniacal silver nitrite produces a bright scarlet precipitate, permanent on boiling. The naphthylamines give no coloration even on warming, but ferric chloride gives a sage-green coloration, which turns brown on heating. On warming with alkalis, the solution becomes pink and eventually dark red, almost chocolate.

o-*Bromobenzenediazohydroxylamino*-p-*toluene*,

$$C_6H_4Br \cdot N{:}N \cdot N(OH) \cdot C_6H_4Me.$$

—o-Bromoaniline was prepared by the reduction of the corresponding nitro-compound according to Fittig and Mager's method (*Ber.*, 1874,

7, 1175). A departure from this method was, however, made in order to isolate the pure substance, dry hydrogen chloride being passed into the dry ethereal solution of the amine, whereby its hydrochloride was precipitated as a pure white solid in an almost theoretical yield.

The diazohydroxylamino-compound crystallises in slender, faintly yellow needles melting at 92°. It is very readily soluble in all the common organic solvents with the exception of alcohol and light petroleum, in which it dissolves rather more sparingly :

0·1455 gave 18·1 c.c. N_2 at 14° and 729 mm. N = 14·03.
0·1279 ,, 0·0780 AgBr. Br = 25·95.
$C_{13}H_{12}ON_3Br$ requires N = 13·73 ; Br = 26·14 per cent.

The substance undergoes slight decomposition on heating with concentrated hydrochloric acid. Ammoniacal silver nitrate is rapidly reduced on warming. Ferric chloride gives a very intense green coloration, and *α*- and *β*-naphthylamines magenta and pinkish-yellow ones respectively.

m-*Bromobenzenediazohydroxylamino*-p-*toluene*,

$$C_6H_4Br\cdot N{:}N\cdot N(OH)\cdot C_6H_4Me,$$

crystallises in very pale yellow, long, striated needles melting at 173°. It is very sparingly soluble in light petroleum or glacial acetic acid, rather more readily so in alcohol, acetone, benzene or ether, and dissolves very easily in chloroform :

0·1480 gave 17·45 c.c. N_2 at 13° and 758 mm. N = 13·90.
0·1361 ,, 0·0836 AgBr ; Br = 26·14.
$C_{13}H_{12}ON_3Br$ requires N = 13·73 ; Br = 26·14 per cent.

The substance is unaffected by hydrochloric acid, but ammoniacal silver nitrate gives a yellow precipitate, which darkens rapidly on warming. Ferric chloride gives a greenish-black coloration, but *α*- and *β*-naphthylamines are without action in the cold, although, on warming, rose-pink and pale yellow colorations are produced, which ultimately become turbid.

p-*Bromobenzenediazohydroxylamino*-p-*toluene*,

$$C_6H_4Br\cdot N{:}N\cdot N(OH)\cdot C_6H_4Me,$$

crystallises in fine hair-like, pale yellow needles melting at 162°. It is very sparingly soluble in light petroleum, alcohol, ether or glacial acetic acid, more readily so in benzene or acetone, and very easily in chloroform :

0·1536 gave 18·1 c.c. N_2 at 13° and 763 mm. N = 13·98.
0·1868 ,, 0·1153 AgBr. Br = 26·26.
$C_{13}H_{12}ON_3Br$ requires N = 13·73 ; Br = 26·14 per cent.

Hydrochloric acid is without action on the substance, but ammoniacal silver nitrate gives a yellow precipitate, which rapidly darkens on heating. Ferric chloride gives an intense bluish-black coloration; α-naphthylamine gives a faint pink colour, which deepens on warming, whilst β-naphthylamine on warming produces a pale yellow coloration.

Work on the stability of these various compounds is approaching completion, and will, it is hoped, form the subject of a further communication at an early date. In conclusion, the authors desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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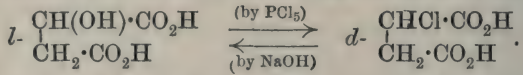
LXXXIX.—*Experiments on the Walden Inversion. Part II. The Interconversion of the Optically Active Mandelic Acids.*

By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

IN a former paper (Trans., 1908, **93**, 811) the authors described a number of experiments bearing on the displacement of chlorine in *l*-phenylchloroacetic acid, $C_6H_5\cdot CHCl\cdot CO_2H$, by the hydroxy- and methoxy-groups. This acid provided an opportunity of investigating a special case of the Walden inversion which had not previously been examined, namely, that of an acid where the halogen is displaced with great readiness and where the large amount of racemisation which accompanies the change is very likely a consequence of the presence of the two electronegative groups, phenyl and carboxyl, directly attached to the asymmetric carbon atom. The action both of water and of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate gave a mixture of *r*- and *l*-mandelic acids, where the preponderance of *r*-acid was very great. On the other hand, the action of water on silver *l*-phenylchloroacetate and the action of silver carbonate on *l*-phenylchloroacetic acid in the presence of water gave a mixture of *r*- and *d*-mandelic acids, the racemisation in this case being less pronounced than in the displacement with the sodium salt. It is thus possible to bring about the interconversion of the enantiomorphously related mandelic acids and to effect the cycle:

$$\begin{tikzcd}
d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \arrow[d, "\text{(by PCl}_5\text{)}"] & d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[l, "\text{(by NaOH)}"'] \\
l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \arrow[r, "\text{(by NaOH)}"] & l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H. \arrow[u, "\text{(by PCl}_5\text{)}"']
\end{tikzcd}$$

In the present state of our knowledge of the Walden inversion, it cannot be said with certainty at which of these stages the change of configuration occurs. At the time of the discovery of the interconversion of the malic acids, the view had been expressed by several chemists that a change of configuration takes place in the transformation of active malic acid into active chlorosuccinic acid by phosphorus pentachloride, the chloro-acid rotating the plane of polarisation in the opposite sense to the particular malic acid used. Walden himself, however, came to the conclusion that in all probability phosphorus pentachloride acts normally. If it is assumed in the case studied by the authors that the action of phosphorus pentachloride is normal, then the action of sodium hydroxide must be taken as abnormal, and the inversion occurs in the displacement of chlorine. One is dealing here with a type of reaction differing in mechanism from that of the type investigated by Walden, who regards the action of sodium hydroxide as normal, since he can effect the following changes, for example:



$$l\text{-}\begin{array}{l}\mathrm{CH(OH)\cdot CO_2H}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{array} \underset{\text{(by NaOH)}}{\overset{\text{(by PCl}_5\text{)}}{\rightleftarrows}} d\text{-}\begin{array}{l}\mathrm{CHCl\cdot CO_2H}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{array}.$$

The view that the action of phosphorus pentachloride on the active mandelic acids is probably normal receives some slight support by analogy with a number of observations made by E. Fischer. Of the reagents used in connexion with the chemistry of the Walden inversion, nitrosyl chloride and bromide are particularly prone to act abnormally when an amino-acid is acted on by them. It seems, however, that the action is normal where the ester of an amino-acid is concerned. *d*-Alanine, for example, is converted into *l*-bromopropionic acid by nitrosyl bromide, whilst ethyl *d*-alanine gives ethyl *d*-bromopropionate. A similar effect has been observed by Fischer with silver oxide, which does not always act abnormally, but does so in certain cases, where the presence of a carboxyl group apparently favours the inversion. Now when phosphorus pentachloride acts on *d*-mandelic acid, the *l*-chloro-acid is formed; when phosphorus pentachloride acts on ethyl *d*-mandelate, ethyl *l*-phenylchloroacetate is formed. Both these actions would thus seem to be normal.

Walden regarded the action of silver oxide in his experiments as abnormal. In the case studied by the authors, however, the parent active mandelic acid is regenerated by the action of silver carbonate and water, thus:

$$d\text{-}\mathrm{C_6H_5\cdot CH(OH)\cdot CO_2H} \underset{\text{(by Ag}_2\text{CO}_3\text{)}}{\overset{\text{(by PCl}_5\text{)}}{\rightleftarrows}} l\text{-}\mathrm{C_6H_5\cdot CHCl\cdot CO_2H}.$$

Two interpretations are possible here: (1) both phosphorus pentachloride and silver carbonate act abnormally, a double Walden inversion taking place, and (2) both phosphorus pentachloride and silver carbonate act normally. We are inclined to take the latter view, although it must be borne in mind that E. Fischer and Scheibler (*Ber.*, 1908, **41**, 889, 2891) have recently submitted evidence from which it appears that a double Walden inversion takes place in certain changes undergone by the optically active α-amino*iso*valeric acids.

Since the behaviour of *l*-phenylchloroacetic acid towards water, sodium hydroxide, and silver carbonate respectively is so different from that of the active halogen succinic acids studied by Walden, it was decided to investigate the action of water and of bases on several of its salts. Walden's results (*Ber.*, 1899, **32**, 1833) may be quoted here for comparison :

Active halogen-succinic acid.	Agent.	Malic acid.
I. *l*-Chlorosuccinic acid	Ag_2O	*l*-Malic acid,* $[\alpha]_D$ about −460°
l-Bromosuccinic ,, ...	H_2O	,, ,, ,, −212
,, ,, ...	TlOH	,, ,, ,, −203
,, ,, ...	HgO	,, ,, ,, −172
,, ,, ...	Hg_2O	,, ,, ,, −130
,, ,, ...	PdO	,, ,, ,, −125
II. ,, ,, ...	Tl_2O_3	*i*-Malic ,, ,, ± 0
III. *l*-Chlorosuccinic ,, ...	RbOH	*d*-Malic ,, ,, +440
,, ,, ...	KOH	,, ,, ,, +425
,, ,, ...	NH_4OH	,, ,, ,, +460
,, ,, ...	CuO	,, ,, ,, +330
l-Bromosuccinic ,, ...	$Cd(OH)_2$	,, ,, ,, +301
l-Chlorosuccinic ,, ...	$Ba(OH)_2$	,, ,, ,, +170
,, ,, ...	$Pb(OH)_2$	,, ,, ,, +170
,, ,, ...	NaOH	,, ,, ,, +150
,, ,, ...	$Sn(OH)_3$	,, ,, ,, +133
,, ,, ...	LiOH	,, ,, ,, +100

* The rotation was intensified in each case by the uranyl nitrate reagent.

The variation in the rotation of the malic acid formed by the different bases is largely due, as Walden suggests, to the experimental conditions being different for each individual base used, so that the active malic acid is nearly always mixed with the *r*-form, the amount of the latter varying within large limits. The displacement of halogen is brought about by two agents, base and water, which, in Class I, act in the same direction to give a malic acid of the same sign as that of the halogen-succinic acid used ; in Class II the effect of water neutralises that of the thallium oxide, whereas in Class III the effects of water and base are opposed to one another.

In the experiments formerly described (*loc. cit.*) on the action of water on *l*-phenylchloroacetic acid, the product was *r*-mandelic acid, but it was suggested that possibly a small amount of active acid might be obtained together with the *r*-acid by variation of the experimental conditions. We now find that a little *l*-mandelic acid can be obtained from the *l*-chloro-acid by means of water, which apparently has the same effect as it had in Walden's experiments in causing an inversion.

The following results were obtained:

Active acid.	Agent.	Sign of rotation of mandelic acid mixture.
l-Phenylchloroacetic acid	Water	*l*-
,, ,,	,, and Ag_2CO_3	*d*-
,, ,,	,, on Ag salt	*d*-
d-Phenylchloroacetic ,,	,, ,, ,,	*l*-
l-Phenylchloroacetic ,,	,, ,, $Hg^{\cdot}$ salt	*d*-
,, ,,	,, ,, $Hg^{\cdot\cdot}$,,	*d*-
,, ,,	,, and $Pd(OH)_2$	*d*-
,, ,,	,, on Na salt	*l*-
,, ,,	,, ,, K ,,	*l*-
,, ,,	,, ,, NH_4 salt	*l*-
,, ,,	,, ,, Li ,,	*l*-
,, ,,	,, ,, Rb ,,	*l*-
,, ,,	,, and CuO	*l*-
,, ,,	,, ,, Cu_2O	*l*-
,, ,,	,, on Ba salt	*l*-
,, ,,	,, ,, $Tl^{\cdot}$,,	*l*-
,, ,,	,, and TlOH on $Tl^{\cdot}$ salt	*l*-
,, ,,	,, ,, NaOH on Na ,,	*l*-
,, ,,	,, on Pb salt	*l*-
,, ,,	,, and Sb_2O_3	*l*-
,, ,,	,, on $Fe^{\cdot\cdot\cdot}$ salt	*l*-
,, ,,	,, and $Pt(OH)_4$	*l*-
,, ,,	,, ,, Na_2CO_3	*l*-

The feature throughout was the large amount of racemisation which accompanied the displacement of halogen. The metals which behave like silver are those which are high in the electromotive series. Platinum is an apparent exception. In the action of platinic hydroxide on the *l*-chloro-acid, however, the preponderating influence is undoubtedly the action of water on the *l*-acid, which gives a slightly lævorotatory mandelic acid mixture. It is quite possible, however, that the action of water on the platinum *l*-salt gives a dextrorotatory mandelic acid mixture, and if this is the case, the effect is counteracted by the preponderance of the *l*-acid formed by the action of water on the *l*-chloro-acid. For the same reason, the examination of the action of the copper oxides and of antimony trioxide was unsatisfactory, inasmuch as two actions were in progress simultaneously, namely, the action of water on the free acid and the action of water on the salt. We do not, therefore, attach much weight to the results obtained in those four cases.

It will be observed that the behaviour of the thallium salt is similar to that of the salts of the alkalis, whereas in Walden's experiments thallium hydroxide behaved like silver oxide.

About the same time as the publication of our first paper on the Walden inversion, E. Fischer and Weichhold (*Ber.*, 1908, **41**, 1286) described the resolution of phenylaminoacetic acid,

$$C_6H_5 \cdot CH(NH_2) \cdot CO_2H,$$

into its optically active components. The active amino-acids were studied with respect to the action of nitrous acid and of nitrosyl bromide on them. The *d*-amino-acid was converted into *r*-mandelic acid by means of nitrous acid, whilst nitrosyl bromide also caused a large amount of racemisation. The conclusion was drawn that, in the elimination of the amino-group from the active phenylaminoacetic acids, there is a great tendency to racemisation, and that the study of the Walden inversion in this particular case is accompanied with special difficulties on this account. Since we had already obtained the *d*- and *l*-phenylchloroacetic acids, the study of the displacement of chlorine in these acids by the amino-group was under consideration, and we are accordingly indebted to the courtesy of Geheimrat Professor Fischer, who agreed to our continuing our work in this direction.

It was found that a change of sign of rotation takes place when the chlorine is displaced by the amino-group. Further, the interconversion of the mandelic acids can be effected by a method different from that described previously, thus:

$$\begin{tikzcd}
d\text{-}C_6H_5 \cdot CH(OH) \cdot CO_2H \arrow[d, "\text{(by } PCl_5)"] & l\text{-}C_6H_5 \cdot CH(NH_2) \cdot CO_2H \arrow[l, "\text{(by } HNO_2)"'] \\
l\text{-}C_6H_5 \cdot CHCl \cdot CO_2H \arrow[d, "\text{(by } NH_4OH)"] & d\text{-}C_6H_5 \cdot CHCl \cdot CO_2H \arrow[u, "\text{(by } NH_4OH)"'] \\
d\text{-}C_6H_5 \cdot CH(NH_2) \cdot CO_2H \arrow[r, "\text{(by } HNO_2)"] & l\text{-}C_6H_5 \cdot CH(OH) \cdot CO_2H. \arrow[u, "\text{(by } PCl_5)"']
\end{tikzcd}$$

The striking feature in each case is the large amount of racemisation which always occurs.

The formation of the amino- from the chloro-acid takes place readily by means of concentrated aqueous ammonia, a certain amount of active mandelic acid being formed at the same time. It is possible to carry out the conversion of the active phenylaminoacetic acids into mandelic acids by means of nitrous acid in such a manner that the racemisation is not complete, and it will be seen from the above scheme that the action is accompanied with a change of sign of rotation.

In the conversion of an active mandelic acid into its enantiomorphous form in the manner indicated, it is exceedingly improbable that a Walden inversion takes place at each of the three stages. The other alternative is that one of the three reagents, phosphorus pentachloride, ammonia, and nitrous acid, acts abnormally. We express the view with reserve, that the inversion takes place by means of the ammonia, whilst phosphorus pentachloride and nitrous acid act normally. Fischer and Scheibler (*loc. cit.*) have already studied a case where ammonia seems to act abnormally. When *d*-valine is acted on by nitrosyl bromide, it forms *l*-bromo*iso*valeric acid, from which by the action of ammonia the original *d*-valine is regenerated. Now if the behaviour of *d*-valine was similar to that of other α-amino-acids, *l*-valine would be formed by the successive action of nitrosyl bromide and ammonia. Fischer and Scheibler quote a number of observations which render it probable that a double Walden inversion took place, that is, that both nitrosyl bromide and ammonia acted abnormally.

The displacement of the amino-group in the active phenylaminoacetic acids by halogen was also examined, and the observation of Fischer and Weichhold (*loc. cit.*), that a large amount of racemisation takes place, was confirmed. Some active halogen acid is, however, produced, and this is opposite in sign of rotation to the amino-acid used. From *l*-phenylaminoacetic acid, for example, a dextrorotatory mandelic acid mixture may be obtained :

$$\begin{tikzcd} l\text{-}C_6H_5\cdot CH(NH_2)\cdot CO_2H \arrow[d, "\text{(by NOBr)}"] & \\ d\text{-}C_6H_5\cdot CHBr\cdot CO_2H \arrow[r, "\text{(by water)}"'] & d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H. \end{tikzcd}$$

Assuming that the behaviour of phenylbromoacetic acid towards ammonia is similar to that of the chloro-acid, the following changes are thus possible :

$$d\text{-}C_6H_5\cdot CHBr\cdot CO_2H \underset{\text{(by NOBr)}}{\overset{\text{(by NH}_4\text{OH)}}{\rightleftarrows}} l\text{-}C_6H_5\cdot CH(NH_2)\cdot CO_2H.$$

It thus appears that the parent active amino-acid can be regenerated by the successive action of nitrosyl bromide and ammonia, an anomalous behaviour which has been observed only with the active valines. Since it is well known that nitrosyl bromide acts abnormally on amino-acids, we think it likely that both ammonia and nitrosyl bromide act abnormally in this transformation, in other words, that a double Walden inversion takes place.

EXPERIMENTAL.

Preparation of d-*Phenylchloroacetic Acid.*

The *l*-phenylchloroacetic acid used in the subsequent experiments was prepared as previously described (*loc. cit.*).

In the course of a series of experiments, conducted with the object of obtaining the *d*-acid, the following observations were made. When an ethyl-alcoholic solution of the *r*-acid was half neutralised with morphine, and the crop which separated on cooling was decomposed in order to remove the morphine, the resulting acid was generally found to be dextrorotatory, but it was occasionally lævorotatory. From a large number of separate experiments, acids of very varying specific rotations in benzene solution were obtained by decomposition of the crystals which separated in each case; the following are some of the figures: +3°, +4·3°, +14·7°, +18°, +114°, +139°, +117°, +168°, +169°, +164°, −9°, −112·9°, −149°, etc.

Since this behaviour affords a very striking example of the influence of temperature and rate of crystallisation on the resolution of a racemic acid, a few details may be given. *r*-Phenylchloroacetic acid (5 grams, 2 mols.) was dissolved in ethyl alcohol (25 c.c.) and morphine (4·5 grams, 1 mol.) was added. The mixture was heated on the water-bath, and the morphine all dissolved before boiling started. The liquid was poured into a beaker surrounded by water at 22°, and stirred vigorously for five minutes, during which time crystallisation took place. The crystals were drained off and amounted to 2·4 grams. After treatment with sodium carbonate, 1·5 grams of morphine were recovered, and this is the amount calculated on the assumption that the salt is composed of 1 mol. of acid and 1 mol. of base. The acid obtained (0·8 gram) was *dextrorotatory*, giving the following value in benzene solution:

$$l=2,\ c=3{\cdot}725,\ \alpha_D\ +8{\cdot}73^\circ,\ [\alpha]_D\ +117{\cdot}2^\circ.$$

In a second experiment, the solution, prepared as before from 5 grams of acid, 25 c.c. of ethyl alcohol, and 4·5 grams of morphine, was surrounded by ice-cold water and not stirred. No crystallisation had set in after thirty minutes. The solution was maintained at about 0° for eight hours longer, by which time crystals had separated. These amounted to 2·1 grams, a little less than in the experiment already quoted. On being decomposed as before, the morphine salt gave 0·7 gram of acid, which was, however, *laevorotatory*, giving the following value in benzene solution: $l=2$, $c=2{\cdot}99$, $\alpha_D\ -8{\cdot}90^\circ$, $[\alpha]_D\ -148{\cdot}8^\circ$. These two experiments were then repeated, and acids of the specific rotations +139·1° and −112·9° respectively were obtained. The experimental conditions were very similar to those adopted previously.

It will thus be seen that conditions can be chosen whereby either a dextrorotatory or a lævorotatory phenylchloroacetic acid is obtained from the crop which separates from a solution of morphine salt made up as described.

Since the immediate object of these experiments was to devise a method for preparing the *d*-acid, we have not continued the work far enough to enable a satisfactory interpretation of this behaviour to be given. Meyerhoffer has pointed out (*Ber.*, 1904, **37**, 2604) that a partially racemic salt is comparable with a double salt in that it possesses three temperature intervals on crystallisation: (*a*) the single salt interval, where the more sparingly soluble single salt crystallises out first, whilst both single salts separate on further crystallisation; (*b*) the transition interval, where the more sparingly soluble single salt crystallises out, whilst the partially racemic salt separates as the crystallisation proceeds, and (*c*) the double salt interval, where only the partially racemic salt separates. A resolution of an acid by the alkaloidal method is possible only in cases (*a*) and (*b*). If this analogy given by Meyerhoffer is borne in mind, it is likely that an adequate explanation of the preceding observations could be provided by a study of the solubility curves of the various morphine salts of the isomeric phenylchloroacetic acids between 0° and 20°.

In some experiments the crystallisation was started from the solution above 20°, and the product then transferred to an ice-chest at 8°. The crystals which separated gave on decomposition an acid which was only slightly dextrorotatory. From 10 grams of *r*-acid, 100 c.c. of ethyl alcohol, and 8·9 grams of morphine, the yield of salt was 7·5 grams, and the resulting acid gave $[\alpha]_D$ +14·7° in benzene solution. In another experiment under similar conditions the acid obtained had $[\alpha]_D + 3°$ in benzene solution.

In another experiment, the crystallisation was conducted slowly at 25°. The solution obtained from 10 grams of *r*-acid, 8·9 grams of morphine, and 50 c.c. of ethyl alcohol was placed in a thermostat at 25°. After two hours, there was no appearance of crystallisation. Next day 6·8 grams of glassy crystals were separated, and the acid prepared from this amount was lævorotatory, giving $[\alpha]_D$ −9° in benzene solution. The filtrate gave an acid with $[\alpha]_D$ +10·9°.

The resolution apparently proceeds differently where methyl alcohol is substituted for ethyl alcohol, and when half the calculated amount of morphine is used as before. Thus the solution obtained from 10 grams of *r*-acid, 8·9 grams of morphine, and 100 c.c. of methyl alcohol was placed, when warm, in an ice-chest at 8°. Crystallisation began after forty-five minutes. Next day the crystals were removed. They amounted to 10·3 grams, and the acid prepared from them was lævorotatory, giving $[\alpha]_D$ −130·1° in benzene solution. The filtrate was also examined, and the acid prepared from it had $[\alpha]_D$ +71·8°. In another experiment where the same quantity of material was used, the crystallisation began before the solution was quite cold and was conducted at 18°. 9·2 Grams of morphine salt were obtained in this case, and the acid had $[\alpha]_D$ −123°, whilst the mother liquor gave an acid with $[\alpha]_D$ +55°.

The pure *d*-acid can be prepared by two methods, as exemplified in the following experiments.

I. The solution obtained from the *r*-acid (50 grams, 1 mol.), morphine (85 grams, 1 mol.), and methyl alcohol (250 c.c.) was allowed to crystallise at 8—10°. After twenty-four hours, the crystals (85 grams) were separated and manipulated as previously described (*loc. cit.*) to obtain the *l*-acid. The mother liquor was allowed to evaporate spontaneously, and the residue treated with sodium carbonate in the usual manner. The acid obtained (17 grams) had $[\alpha]_D$ +111° for $c = 3{\cdot}75$ in benzene solution. It was dissolved in 50 c.c. of ethyl alcohol, and morphine (14 grams) added in amount necessary for half neutralisation. The mixture was heated until the morphine dissolved, and was then surrounded by water at 22°; it was stirred for five minutes to start the crystallisation, and then allowed to remain at 22° for ten minutes longer. The crop which separated amounted to 10 grams, and from it there were obtained 3 grams of acid which was nearly pure, giving $[\alpha]_D$ +188·5° for $c = 3{\cdot}746$ in benzene solution. After one crystallisation from low-boiling light petroleum the acid is pure.

II. It has already been shown that when the *r*-acid is half neutralised by morphine in ethyl-alcoholic solution the morphine salt which separates gives a very active acid if the crystallisation is conducted with stirring at 22°. But the acid mixture was not sufficiently active to enable the separation of the pure acid from this mixture by crystallisation with light petroleum to be practical. For this purpose it is necessary to obtain an acid mixture with an activity of at least $[\alpha]_D$ 140° in benzene solution. The following method gave the result desired:

The *r*-acid (10 grams) was dissolved in 100 c.c. of ethyl alcohol and morphine (9 grams) added. The mixture was warmed until the solution of the morphine was complete. Crystallisation began when the solution was cooling. The mixture was maintained at 16—18° for twenty-four hours. The crystals which separated amounted to 7 grams, and from them 2·3 grams of acid with the rotation $[\alpha]_D$ +164·3° for $c = 1{\cdot}57$ in benzene solution were obtained. The pure acid was obtained after two crystallisations from low-boiling light petroleum.

d-*Phenylchloroacetic acid*, $C_6H_5{\cdot}CHCl{\cdot}CO_2H$, like the *l*-acid, melts at 60—61°. On analysis:

Found, Cl = 20·8. $C_8H_7O_2Cl$ requires Cl = 20·8 per cent.

Its rotation was determined in benzene solution:

$$l = 1,\ c = 1{\cdot}935,\ \alpha_D^{16}\ +3{\cdot}70°,\ [\alpha]_D^{16}\ +191{\cdot}2°.$$

The value previously obtained for the *l*-acid was $[\alpha]_D^{12}$ $-191°$ for $c = 3{\cdot}345$ in benzene solution.

It may be mentioned that the *l*-acid underwent no appreciable autoracemisation in the course of one and a-half years, during which time it was preserved in a stoppered tube in the dark (compare Walden, *Ber.*, 1898, **31**, 1416).

Conversion of l-*Phenylchloroacetic Acid into a Mixture of* r- *and* l-*Mandelic Acids.*

The displacement of halogen in *l*-phenylchloroacetic acid was conducted under a variety of conditions, and was complete in each case. The active mandelic acid mixtures obtained were examined in ethylalcoholic solution.

Action of Water on l-*Phenylchloroacetic Acid.*—It had previously been observed that the complete displacement of halogen in *l*-phenylchloroacetic acid takes place with great readiness at 100°, but the resulting mandelic acid was found to be inactive in these experiments. A mixture of *r*- and *l*-mandelic acids is, however, easily obtained by the action of water at 25° on the *l*-chloro-acid, but the proportion of *l*-mandelic acid in the mixture is very small.

The velocity of displacement of chlorine in *r*-phenylchloroacetic acid was roughly measured at 25°. The acid (0·852 gram) was dissolved in 100 c.c. of water by shaking in a thermostat at 25°. After three days, 10 c.c. of the solution required 14·9 c.c. of $0{\cdot}053N$ aqueous sodium hydroxide for neutralisation; after six days, 17·0 c.c. of alkali were required; after eight days, 17·8 c.c.; after ten days, 18·0 c.c.; after thirteen days, 18·3 c.c. The displacement by this time was nearly complete, since, on boiling the latter solution, an additional 0·7 c.c. of alkali was required for neutralisation.

l-Phenylchloroacetic acid (0·85 gram) was accordingly dissolved in 100 c.c. of water, and the solution maintained at 25° for twenty days, at the end of which time 10 c.c. required 18·5 c.c. of $0{\cdot}053N$ aqueous sodium hydroxide for neutralisation. The latter solution (28·5 c.c.) was then heated at 100° for thirty minutes, when an additional 0·5 c.c. of alkali was required for neutralisation; the solution remained neutral after additional heating for thirty minutes. The remaining 90 c.c. of solution were therefore heated at 100° for one hour, and the solution was then found to be lævorotatory. The mandelic acid mixture (0·6 gram) extracted from it gave $l = 4$, $c = 2{\cdot}248$, α_D $-0{\cdot}28°$, $[\alpha]_D$ $-3{\cdot}1°$

Action of Water on Potassium l-*Phenylchloroacetate*.—*l*-Acid (0·6 gram); water (10 c.c.); neutralised by potassium hydroxide; solution (35 c.c.) at the ordinary temperature for fourteen days, then at 100° one hour. The resulting mandelic acid mixture (0·4 gram) had $[\alpha]_D - 3·8°$ for $c = 1·448$.

Action of Water on Ammonium l-*Phenylchloroacetate*.—*l*-Acid (0·5 gram); water (10 c.c.); neutralised by ammonia; solution (50 c.c.) at the ordinary temperature for twelve days; concentrated to 33 c.c., 20 c.c. of which in a 4-dcm. tube gave $\alpha_D - 0·28°$. The resulting mandelic acid mixture gave $[\alpha]_D - 5·0°$ for $c = 1·2475$.

Action of Water on Lithium l-*Phenylchloroacetate*.—*l*-Acid (0·5 gram); water (25 c.c.); neutralised by lithium hydroxide; solution (50 c.c.) at the ordinary temperature for twelve days; boiled for thirty minutes. The resulting mandelic acid was lævprotatory, $[\alpha]_D - 3·3°$ for $c = 1·766$.

Action of Water on Rubidium l-*Phenylchloroacetate*.—*l*-Acid (0·5 gram); water (25 c.c.); neutralised by rubidium hydroxide; solution (50 c.c.) at the ordinary temperature for twelve days; boiled for thirty minutes. Solution (31 c.c.) was lævorotatory, 20 c.c. of it in a 4-dcm. tube giving $\alpha_D - 0·29°$. The mandelic acid mixture gave $[\alpha]_D - 3·8°$ for $c = 1·7925$.

Action of Cupric Oxide on l-*Phenylchloroacetic Acid*.—Freshly precipitated cupric oxide from 0·4 gram of copper sulphate, suspended in water (25 c.c.), and added to 0·5 gram of *l*-acid dissolved in 25 c.c. of water; at 60°, one hour; the copper oxide dissolved; one hour at 100°; dilute hydrochloric acid added; copper removed by hydrogen sulphide. The resulting mandelic acid gave $[\alpha]_D - 3·0°$ for $c = 1·412$.

Action of Cuprous Oxide on l-*Phenylchloroacetic Acid*.—Cuprous oxide, prepared from 5 grams of copper sulphate, added to solution of 1 gram of *l*-acid in 50 c.c. of water; twenty-four hours at the ordinary temperature; 60°, one hour; 100°, one hour; copper removed. Acid gave $[\alpha]_D - 7·7°$ for $c = 2·665$.

Action of Water on Barium l-*Phenylchloroacetate*.—*l*-Acid (0·5 gram); water (10 c.c.); neutralised by aqueous barium hydroxide; solution (50 c.c.) at the ordinary temperature for twelve days; concentrated to 22 c.c., which gave $\alpha_D - 0·5°$ in a 4-dcm. tube. The acid gave $[\alpha]_D - 5·1°$ for $c = 1·28$.

Action of Thallous Hydroxide on Thallous l-*Phenylchloroacetate*.—*l*-Acid (0·5 gram, 1 mol.); water (25 c.c.), and 41 c.c. of an aqueous solution of thallous hydroxide (2 mols.); four days at the ordinary temperature; 60°, one hour; 100°, thirty minutes; concentrated to 50 c.c., and the mandelic acid extracted after separation of the thallous chloride. The specific rotation was $[\alpha]_D - 3·7°$ for $c = 1·16$.

The action of water on thallous *l*-phenylchloroacetate also gave a similar result; a mandelic acid mixture with $[\alpha]_D$ −5·1° for $c = 2·31$ having been obtained.

Action of Water on Lead l-*Phenylchloroacetate.*—The lead salt, prepared from 0·85 gram of the *l*-acid by the addition of lead acetate to the sodium salt, shaken for one hour with 50 c.c. of cold water; after twenty-five hours warmed at 40° for five hours, a preliminary experiment having shown that the displacement of the chlorine is complete under these conditions; lead removed by hydrogen sulphide; the filtrate (65 c.c.) was lævorotatory, 20 c.c. of it in a 4-dcm. tube giving α_D −0·36°. The resulting mandelic acid mixture gave $[\alpha]_D$ −5·5° for $c = 1·19$.

Action of Antimony Trioxide on l-*Phenylchloroacetic Acid.*—*l*-Acid (0·5 gram, 1 mol.), dissolved in water (50 c.c.), and antimony trioxide (0·4 gram, ½ mol.) added; at the ordinary temperature for thirty minutes; 60°, two hours; 100°, one hour. Some of the antimony oxide had dissolved. The antimony was removed by hydrogen sulphide, and the mandelic acid gave $[\alpha]_D$ −4·3° for $c = 1·41$.

Action of Water on Ferric l-*Phenylchloroacetate.*—Ferric *l*-salt, prepared from acid (0·5 gram) by the addition of ferric chloride to the sodium salt, added to water (100 c.c.); at the ordinary temperature for twenty-four hours; 60°, five hours; the product gave a mandelic mixture, which, as usual, was free from chlorine and gave $[\alpha]_D$ −10·3° for $c = 1·11$.

Action of Platinic Hydroxide on l-*Phenylchloroacetic Acid.*—Platinic hydroxide (0·4 gram) added to solution of the *l*-acid (1 gram) in water (50 c.c.); eighteen days at the ordinary temperature; 100°, two hours. Practically all the platinic hydroxide dissolved during the heating. The platinum was removed from the yellow solution by hydrogen sulphide. The resulting acid gave $[\alpha]_D$ −4·3° for $c = 3·62$.

Action of Water and Sodium Carbonate on Sodium l-*Phenylchloroacetate.*—*l*-Acid (1 gram); 20 c.c. of *N*/1 sodium carbonate; forty-five hours at the ordinary temperature; 40°, two hours; 100°, thirty minutes. The resulting mandelic acid gave $[\alpha]_D$ −7·2° for $c = 3·77$.

Conversion of l-*Phenylchloroacetic Acid into a Mixture of* r- *and* d-*Mandelic Acids.*

Action of Water on Mercuric l-*Phenylchloroacetate.*—Freshly precipitated mercuric oxide from 0·4 gram of mercuric chloride, suspended in water, and gradually added with shaking to 0·5 gram of the *l*-acid and 25 c.c. of water. The liquid (70 c.c.) was then shaken at the ordinary temperature for fifteen minutes until nearly all the oxide had dissolved; after twenty-four hours, heated at 50° for five hours. The mercury was removed by hydrogen sulphide. The filtrate (65 c.c.) was dextrorotatory, 20 c.c. of it in a 4-dcm. tube giving α_D $+0{\cdot}21°$. The resulting mandelic acid mixture gave $[\alpha]_D$ $+11{\cdot}1°$ for $c=1{\cdot}54$.

Action of Water on Mercurous l-*Phenylchloroacetate.*—The mercurous salt, prepared by the addition of aqueous mercurous nitrate to the sodium salt obtained from 0·5 gram of the *l*-acid, was shaken with 30 c.c. of water for fifteen minutes; after twenty-five hours, heated at 50° five hours; after twenty hours, the mercurous chloride was filtered off and washed with water. The filtrate (35 c.c.), which gave no precipitate on the addition of hydrochloric acid, was dextrorotatory, 20 c.c. of it in a 4-dcm. tube giving α_D $+1{\cdot}64°$. The mandelic acid mixture gave $[\alpha]_D$ $+41{\cdot}2°$ for $c=1{\cdot}05$.

Action of Palladous Hydroxide on l-*Phenylchloroacetic Acid.*—Palladous hydroxide, obtained from palladous chloride (0·3 gram), was suspended in water (50 c.c.) and gradually added to a solution of 0·6 gram of the *l*-acid in 50 c.c. of water; eighteen hours at the ordinary temperature; some of the palladous hydroxide had dissolved. The solution was nearly complete after heating at 60° for fifteen minutes; maintained at 60° three hours; at 100° thirty minutes. The palladium was removed as sulphide, and the filtrate (25 c.c.) was dextrorotatory, giving α_D $+1{\cdot}0°$ in a 4-dcm. tube. The resulting mandelic acid mixture gave $[\alpha]_D$ $+9{\cdot}7°$ for $c=2{\cdot}17$.

Conversion of d-*Phenylchloroacetic Acid into a Mixture of* r- *and* l-*Mandelic Acids.*

d-Acid (0·8 gram), added to 5 c.c. of water, and neutralised exactly by standard aqueous sodium hydroxide (43·6 c.c.). After addition of 47 c.c. of *N*/10 silver nitrate, 8—10° forty-seven hours; 100°, ten minutes. A little dilute hydrochloric acid was added, the silver chloride separated, and the filtrate concentrated by evaporation to about 25 c.c. The mandelic acid mixture gave $[\alpha]_D$ $-41{\cdot}5°$ for $c=2{\cdot}23$.

Conversion of l-*Phenylchloroacetic Acid into a Mixture of* r- *and* d-*Phenylaminoacetic Acids.*

l-Phenylchloroacetic acid (3 grams) was added to 50 c.c. of strong ammonia (sp. gr. 0·880) which had previously been cooled by ice. The acid dissolved at once. The solution was surrounded by ice for six hours, and, after eighty-six hours at a temperature varying from 12° to 14°, it was heated for thirty minutes at 60° and finally for thirty minutes at 100°. It was then evaporated to dryness to expel the ammonia. Water (50 c.c.) was added, the mixture heated on the water-bath, and the crop, which separated on cooling, washed with ice-cold water. The amino-acid obtained in this manner amounted to

0·9608 gram. It was dissolved in 12·8 c.c. of 0·99N hydrochloric acid, and the solution, when made up to 50 c.c., was polarimetrically examined with the result:

$$l=4,\ \alpha_D\ +4{\cdot}65°,\ [\alpha]_D\ +60{\cdot}5°.$$

The filtrate from which this crop had been removed was concentrated to about 25 c.c., when a small amount of amino-acid separated on cooling. This was considerably more active than the first crop; 0·1435 gram was dissolved in 2 c.c. of N-aqueous hydrochloric acid and water, and made up to 20 c.c. with water. On polarimetric examination, it gave:

$$l=2,\ \alpha_D\ +1{\cdot}99°,\ [\alpha]_D\ +139°.$$

Dilute hydrochloric acid was added to the filtrate from which this crop had been removed and the liquid extracted with ether. In this manner, 1 gram of a lævorotatory mandelic acid mixture was obtained with the following rotation:

$$l=2,\ c=4{\cdot}625,\ \alpha_D\ -2{\cdot}80°,\ [\alpha]_D\ -30{\cdot}3°.$$

The solution of amino-acid hydrochloride from which the mandelic acid had been extracted was evaporated to 23 c.c. and was dextrorotatory, 20 c.c. of it in a 4-dcm. tube giving $\alpha_D+1{\cdot}92°$.

It is thus apparent that the action of ammonia on *l*-phenylchloroacetic acid gives a dextrorotatory mixture of amino-acids, but the racemisation accompanying the change is in this case not nearly so pronounced as when the chlorine is displaced by the hydroxy-group. The formation of mandelic acid together with the amino-acids is presumably due to the action of water and excess of ammonia on ammonium *l*-phenylchloroacetate, and it is interesting to note that the presence of an excess of ammonia has the effect of giving a mandelic acid mixture of fairly high activity.

Conversion of d-*Phenylchloroacetic Acid into a Mixture of* r- *and* l-*Phenylaminoacetic Acids.*

d-Phenylchloroacetic acid (2 grams) was added to 50 c.c. of strong ammonia (sp. gr. 0·880), and the solution maintained at 8—10° for three days. After heating at 40° for thirty minutes and at 100° for thirty minutes, the product was evaporated to dryness. About 25 c.c. of water were added, the mixture heated on the water-bath, cooled, and filtered. The solid was washed with a little water, and, on being dried, amounted to 0·8 gram. It was lævorotatory. 0·5615 Gram was added to water and 10 c.c. of N-aqueous hydrochloric acid, and the solution made up with water to 25 c.c.

On polarimetric examination:

$$l=4,\ \alpha_D\ -4{\cdot}32°,\ [\alpha]_D\ -48{\cdot}1°.$$

Dilute hydrochloric acid was added to the filtrate from which the preceding crop had been removed, and the mandelic acid present was separated from the amino-acid hydrochloride by extracting twice with ether. It amounted to 0·5 gram, was dextrorotatory, and gave the following value:

$$l=4,\ c=2{\cdot}4075,\ a_D\ +2{\cdot}21^\circ,\ [a]_D\ +23^\circ.$$

The liquid which had been extracted was evaporated to 23 c.c., 20 c.c. of which in a 4-dcm. tube gave $a_D\ -4{\cdot}32^\circ$.

Action of Nitrous Acid on the Optically Active Phenylaminoacetic Acids.

The optically active phenylaminoacetic acids were prepared by the resolution of the *r*-acid as described by E. Fischer and Weichhold (*loc. cit.*). The inactive acid was converted into its formyl derivative, which was then resolved by cinchonine; from the *l*-formyl phenylaminoacetic acid thus obtained, the formyl group was eliminated by aqueous hydrobromic acid. The activity of the resulting *l*-phenylaminoacetic acid was in close agreement with the value quoted by Fischer and Weichhold, who give the following data: 0·7438 gram of acid was dissolved in 6·7 c.c. of *N*-hydrochloric acid and 3 c.c. of water; a_D^{20} was $-23{\cdot}35^\circ$ in a 2-dcm. tube and $[a]_D^{20}-157{\cdot}78^\circ$. The value obtained by us was as follows: 0·7438 gram of acid was dissolved in 6·1 c.c. of 1·1*N*-hydrochloric acid and 3·6 c.c. of water; a_D was $-11{\cdot}65^\circ$ in a 1-dcm. tube.

The following experiment showed that a small amount of *d*-mandelic acid is produced together with the *r*-acid by the action of nitrous acid on *l*-phenylaminoacetic acid hydrochloride. A solution of 2 grams of the *l*-amino-acid in 50 c.c. of 1·1*N*-aqueous hydrochloric acid was surrounded by ice-cold water, and an aqueous solution of sodium nitrite (1·9 grams dissolved in 4 c.c. of water) gradually added within an interval of forty-five minutes. The solution was shaken occasionally. After remaining for five and three-quarter hours in ice-cold water without shaking, the solution was polarimetrically examined and found to be lævorotatory, 20 c.c. of it in a 4-dcm. tube giving $a_D\ -1{\cdot}65^\circ$. On shaking the solution at this stage, a little gas was evolved, and the action was apparently not quite complete. After sixteen hours at the laboratory temperature, the evolution of gas had ceased, and the solution had become dextrorotatory. Two days later, 20 c.c. of the solution gave $a_D\ +0{\cdot}40^\circ$ in a 4-dcm. tube, and the mandelic acid mixture, when extracted, amounted to 1·61 grams and gave the following value:

$$l=4,\ c=8{\cdot}05,\ a_D\ +1{\cdot}75^\circ,\ [a]_D\ +5{\cdot}4^\circ.$$

A similar experiment was carried out with *d*-phenylaminoacetic acid, which was prepared by resolution of the formyl acid with quinine as described by Fischer and Weichhold (*loc. cit.*). The mandelic acid mixture, produced by the action of nitrous acid, was lævorotatory, giving $[\alpha]_D$ $-7{\cdot}3°$.

Conversion of the Optically Active Phenylaminoacetic Acids into Phenyl-halogen-acetic Acids.

A solution of 5·5 grams of *l*-phenylaminoacetic acid in 100 c.c. of aqueous hydrobromic acid (40 per cent.) was immersed in a freezing mixture of ice and salt, and 9 grams of bromine were added. After a current of nitric oxide had been passed into the mixture for one and a-half hours, an additional 13 grams of bromine were added, and the passage of nitric oxide continued for three and a-half hours longer. The evolution of nitrogen was noticed. Next day a current of sulphur dioxide was passed into the mixture, which was then extracted with ether. The resulting acid was neutralised by aqueous sodium hydroxide, and the heating of the aqueous solution of sodium salt conducted for some time in order to displace the halogen from the bromo-acid. Finally, the mandelic acid was obtained from the sodium salt. Its aqueous solution (60 c.c.) was dextrorotatory, 20 c.c. of it in a 4-dcm. tube giving α_D $+0{\cdot}44°$.

The displacement of the amino-group in *d*-phenylaminoacetic acid by the halogen atom was conducted under conditions which were different from the preceding. The acid used was not homogeneous, as it contained some of the *r*-acid and had $[\alpha]_D$ $+119°$ in hydrochloric acid solution of the same strength as was used for the determination of the activity of the *l*-acid. The acid (1 gram) was added to 20 c.c. of concentrated aqueous hydrochloric acid. A solution of 0·8 gram of sodium nitrite in 3 c.c. of water was gradually added within an interval of thirty minutes. After one and a-half hours, there was no further evolution of gas, and some sodium chloride had separated. The liquid was extracted with ether, the ethereal extract dried, the ether expelled, and an oil obtained, which quickly solidified in a vacuum. It amounted to 0·88 gram, and from its melting point (55—65°) seemed to consist mainly of a mixture of *r*- and active phenylchloroacetic acids. It was made up with benzene to 20 c.c., and, after shaking, 0·4 gram remained undissolved and was found from its melting point to be *r*-mandelic acid. The portion soluble in benzene was examined. It was *laevorotatory*, giving $[\alpha]_D$ $-21{\cdot}4°$ for $c=4{\cdot}2$ in benzene solution. The displacement of the amino-group by chlorine is thus accompanied by a change of sign. This observation was confirmed by the behaviour of the product towards ammonia. The residue, obtained after removal of the benzene, was dissolved in

25 c.c. of concentrated aqueous ammonia and maintained at about 8° for twenty-four hours. The liquid was then concentrated by evaporation on the water-bath to about 10 c.c., an excess of dilute hydrochloric acid added, and the product extracted with ether. The resulting acid (0·32 gram) was lævorotatory, and was a mixture of *r*- and *l*-mandelic acids with $[\alpha]_D$ −8·0° for $c = 1·595$. The liquid which had been extracted was distinctly dextrorotatory.

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XC.—*Indican. Part II.*

By ARTHUR GEORGE PERKIN and FREDERICK THOMAS.

IN a previous communication (Trans., 1907, **91**, 1715), it was shown that indican, the glucoside of indoxyl which is present in certain plants which yield indigo, can be readily extracted from the leaf by means of acetone, and isolated in quantity by an exceedingly simple method. For the purpose of further investigation, an amount approximating to 350 grams of the crude, crystalline glucoside was prepared according to this process by the authors in conjunction with W. P. Bloxam, and this, it was found, could be readily purified by crystallisation from absolute alcohol. The product, which was of about 94 per cent. purity (calculated as $C_{14}H_{17}O_6N,3H_2O$), was added to three times its bulk of the alcohol, dissolved by very gentle warming, filtered from a trace of indigotin, and the solution partly evaporated. The crystals, which separated on cooling, were again recrystallised from alcohol, and were now usually quite colourless and chemically pure. From the mother liquors, by evaporation, a further amount of the substance could be recovered, and it was thus evident that indican suffers little or no decomposition in boiling absolute alcoholic solution:

Found, $C = 56·89$; $H = 5·80$; $N = 4·83$.

$C_{14}H_{17}O_6N$ requires $C = 56·94$; $H = 5·76$; $N = 4·75$ per cent.

In order, however, to be certain as to the purity of the substance, determinations were carried out by the new isatin method of Orchardson, Wood, and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 4) as certain of the samples came to hand:

0·1181	gave	0·1050	indirubin	100 per cent.	Theory requires	0·1048	gram.
0·1052	,,	0·0930	,,	,,	,, ,,	0·0935	,,
0·1015	,,	0·0900	,,	,,	,, ,,	0·0901	,,
0·1134	,,	0·1000	,,	,,	,, ,,	0·1007	,,

On the other hand, some preparations of the indican were, for economy's sake, merely crystallised once from alcohol, and the product thus obtained was employed in this investigation for experiments where absolute purity of the substance was not essential. When such was the case, this is referred to in connexion with the experiment.

During the preparation of the indican, a considerable quantity of the aqueous mother liquor accumulated, which, on keeping, gradually darkened, and after some time developed a peculiar odour closely resembling that of acridine. An examination was carried out of the freshly prepared product to determine if any indication could be obtained of the presence of an indoxyl glucoside other than indican. One of the most ready methods of eliminating the large quantity of impurity present was found to consist of the addition of ether to an alcoholic solution of the mixture, and to evaporate the clear liquid containing most of the indoxyl glucoside in a vacuum. As a result of the fractional crystallisation of the residue from water, crystals of indican only were obtained, and no new glucoside of this character has been yet brought to light.

Prof. ter Meulen (*private communication*) has confirmed the suggestion (*loc. cit.*) that the melting point, 51°, given in the paper of Hoogewerff and ter Meulen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 520) is a clerical error, and is in reality intended for 57°. The same chemist also directed attention to a paper by himself, "*Recherches expérimentales sur la nature de quelques glucosides*" (*Rec. trav. chim.*, 1905, **24**, 444), containing some experiments on indican of which we were unaware. An interesting modification of the original method for the isolation of this glucoside from *Polygonum tinctorium* is there given, and consists in treating a cold solution of the partly purified substance with sulphuric acid, by which means certain impurities are precipitated, remarkably enough without a perceptible hydrolysis of the indican itself. The acid is then removed by barium carbonate, and from the solution the crystalline compound readily separates.

The main object of this communication of ter Meulen's is, in so far as it concerns indican, the determination of the sugar that this glucoside yields when hydrolysed by its specific enzyme, and as a result it is shown that whereas the hydrolysis proceeds readily in the presence of galactose, saccharose, and mannose, and a yield of indoxyl approximating 93 per cent. is thus produced, that the reaction is inhibited by the presence of glucose to some extent, as but 86·4 per cent. of indoxyl is obtained. The sugar produced is therefore dextrose, and this was confirmed by the isolation of the pure sugar and its osazone melting at 202—203°. In the meantime, a further study of the sugar had been in progress in this laboratory, owing to the fact that the melting point of pure dextrosazone has been given by Tutin (Proc., 1907, **23**, 250) as 217°, whereas in the former communication the product obtained melted at 204—205°. A quantity of the pure sugar from indican was prepared and purified by crystallisation from methyl alcohol, but on conversion into the osazone and by crystallising this substance from various solvents, no higher melting point than 204—205° could be observed when the heating was carried out with moderate rapidity. An examination of pure dextrose in this respect gave a similar result. As a final confirmation, the sugar from indican was acetylated by Erwig and Koenigs' method (*Ber.*, 1889, **22**, 1464), and the purified compound compared with acetyldextrose. Both preparations melted at 109—110°, and a mixture of the two behaved in an identical manner.

It has been shown by Baeyer (*Ber.*, 1881, **14**, 1745) that indoxyl readily condenses with aldehydes and ketones to form the so-called indogenides, and Hazewinkel (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512), in the valuable communication which demonstrated for the first time that indican is an indoxyl glucoside, partly identified his substance by means of its condensation products with isatin, benzaldehyde, and pyruvic acid, relying, however, on their qualitative reactions, as he did not prepare these compounds in a pure enough condition for analysis. In connexion with the analysis of crystalline indican, and the amount of this compound which is present in the plant, it is now well known that the interaction of indoxyl and isatin to form indirubin is the basis of a method which, when carefully carried out, gives remarkably accurate results (*loc. cit.*). It was, however, interesting to determine if certain aldehydes could be usefully employed to replace the isatin in this process, and as it was necessary that the final product of the reaction, like indirubin, should be insoluble in dilute alkali, *p*-nitrobenzaldehyde and piperonal were selected for experiment.

When 1 gram of indican was dissolved in 30 c.c. of water, the solution treated with 1 gram of *p*-nitrobenzaldehyde, and heated to boiling in the absence of air, the addition of 5 c.c. of hydrochloric acid caused the almost instantaneous separation of a red, crystalline mass. After recrystallisation from acetone, it melted at 273—274°, dissolved sparingly in ether to form a beautiful green, fluorescent liquid, and was identical with the *p*-nitrobenzaldehydeindogenide previously described by Baeyer (*loc. cit.*):

Found, N = 10·60. $C_{15}H_{10}O_3N_2$ requires N = 10·52 per cent.

Experiment indicated the extreme readiness with which this reaction occurs, for with indican solution at a dilution of 1 in 1000, the above compound quickly separates, and even at 1 in 10,000 of water the condensation can be observed to take place. As a result of the study of the quantitative aspect of the process, the following method was devised. 0·25 Gram of indican (99 per cent.), dissolved in 150 c.c. of water, was treated with 0·75 gram of *p*-nitrobenzaldehyde, the mixture heated to boiling in an atmosphere of carbon dioxide, and treated drop by drop with 5 c.c. of hydrochloric acid diluted with 25 c.c. of water. After digestion for half an hour, 250 c.c. of boiling water were added for the purpose of retaining the excess of aldehyde in solution, and the product was then boiled for ten minutes longer, cooled, and kept for half an hour. The crystals were collected on a tared filter, washed with water, then with 0·5 per cent. sodium hydroxide solution, and finally with warm 4 per cent. acetic acid:

Found, 0·2229 gram. Theory requires 0·2231 gram. Yield = 99·91 per cent.
„ 0·2225 „ „ „ 0·2231 „ Yield = 99·73 „

It was accordingly evident that the condensation of indoxyl with *p*-nitrobenzaldehyde takes place under these conditions in a quantitative manner. The product thus obtained was quite free from the aldehyde, melted at 273—274°, and was therefore pure.

The interaction of piperonal with indoxyl, which does not appear to have been previously studied, readily takes place under similar conditions to those employed with *p*-nitrobenzaldehyde. A voluminous, orange-coloured, crystalline mass quickly separates, and the product is purified by crystallisation from alcohol:

Found, $C=72·37$; $H=4·34$; $N=5·46$.

$C_{16}H_{11}O_3N$ requires $C=72·45$; $H=4·15$; $N=5·28$ per cent.

The new compound consists of needles, melting at 223—224°, sparingly soluble in ether, with formation of a green, fluorescent solution.

Piperonal does not react with indoxyl quite so readily as *p*-nitrobenzaldehyde, for although the condensation takes place to some extent with a mixture of 1 gram of indican, 1 gram of the aldehyde, and 10 c.c. of hydrochloric acid in 1000 c.c. of boiling water at a dilution of 1 in 10,000, no production of the expected compound could be observed.

As a result of the quantitative study of this process, the following method has as yet given the best result. 0·25 Gram of 99 per cent. indican in 250 c.c. of water, 0·75 gram of piperonal, and 5 c.c. of hydrochloric acid were caused to react under identical conditions with those employed in the *p*-nitrobenzaldehyde experiments, with the exception that the digestion was carried out for one hour:

Found, 0·2132 gram. Theory requires 0·2221 gram. Yield = 96 per cent.
„ 0·2130 „ „ „ 0·2221 „ Yield = 95·90 „

The employment of piperonal for the quantitative estimation of indican thus yields under these conditions but approximately satisfactory results, and this appears to be due to the fact that the acid filtrate retains a small amount of the condensation product in solution. The crystals, which were of a dull orange colour, melted at 217—219°, and were evidently not quite pure; and again, although the piperonal is to some extent dissolved by the water, and much is driven off with the steam during the reaction, a trace is apt to be retained by the substance, and prolonged heating of this at 100° is necessary until the characteristic odour of the aldehyde has disappeared. *o*- and *m*-Nitrobenzaldehydes readily react when treated with indican under similar conditions, and it is possible that the crystalline compounds thus produced might be serviceable for the estimation of this glucoside.

p-Nitrobenzaldehyde and piperonal respectively form the above compounds when they are digested with aqueous extracts of the leaves of *I. Sumatrana* and *I. arrecta* in the presence of hydrochloric acid. Crystalline precipitates rapidly separate, and these were collected and washed with 0·5 per cent. slightly warm sodium hydroxide solution, which removed a brown impurity. The *p*-nitrobenzaldehydeindogenide thus obtained was of a bright red colour, melted at 264—265°, and was almost pure, whereas the piperonal derivative had a dull orange colour, and crystallisation from alcohol was necessary in order to obtain it in a pure condition.

It is thus likely that *p*-nitrobenzaldehyde can be employed as well as isatin for the estimation of indican in the leaf, but as *p*-nitrobenzaldehydeindogenide is slightly more sensitive to sodium hydroxide solution than indirubin, the alkaline washing which is necessary should be carried out with a very dilute and merely warm solution. A point which should be in favour of the method is the extreme rapidity with which the operations of filtration and washing can be carried out.

As a side issue in connexion with this portion of the work, it appeared interesting to study the condensation product of indoxyl with protocatechualdehyde, as the resulting dihydroxybenzaldehydeindogenide should possess mordant dyeing properties. Somewhat unexpected difficulties were at first encountered in the preparation of this substance, because, although it was present in the experimental products, it was so largely contaminated with a brown impurity that its isolation was extremely difficult. This brown compound apparently arises from a decomposition of the colouring matter itself, and an illustration of this point occurs when protocatechualdehyde and indican dissolved in acetic acid are treated with a little hydrochloric acid and gently warmed. Thus the substance at first formed is soluble in alkali with a bluish-violet coloration, but on raising the temperature an alkaline solution of the product has now merely a deep brown tint. The following method was finally adopted. Two grams of indican * and 2 grams of protocatechualdehyde, dissolved in 30 c.c. of boiling alcohol, were treated with 8 drops of hydrochloric acid, and the orange-brown liquid at once removed from the sand-bath and kept for twenty-four hours. Crystals had then separated, and after addition of a little hot water, the substance was collected and washed with alcohol. The yield was 0·69 gram of the crude product, and this was purified by evaporating its alcoholic solution until crystals separated from the boiling liquid:

Found, C = 70·92; H = 4·40; N = 5·55.
$C_{15}H_{11}O_3N$ requires C = 71·14; H = 4·35; N = 5·53 per cent.

Dihydroxybenzaldehydeindogenide consists of glistening, orange-red needles resembling alizarin, melts at about 264—265°, and dissolves very sparingly in ether, with formation of a green, fluorescent liquid. Its behaviour with alkaline solutions is interesting, for whereas concentrated sodium hydroxide gives a beautiful bluish-violet coloration, with the weaker alkali and also with concentrated ammonia a red tint only is produced. Alcohol dissolves it without fluorescence, with sulphuric acid it gives an orange-red colour, with ferric chloride a dull purplish-red tint, and with alcoholic lead acetate a bright orange-red precipitate. A concentrated boiling alcoholic solution gives with potassium acetate a red deposit, consisting of ill-defined, prismatic needles, and this compound, which is probably the monopotassium salt, is soluble in alcohol, and on boiling with water is decomposed with regeneration of the free colouring matter. With sulphuric acid in boiling glacial acetic acid, a bluish-black, crystalline powder is formed, and this, on treatment with cold water, is re-converted into the free acid and the original compound, at least in part.

The *acetyl* derivative, $C_{15}H_9O_3N(C_2H_3O)_2$, is quickly formed by a short digestion of the colouring matter with acetic anhydride and a few drops of pyridine. It separates on cooling, and is purified by recrystallisation from alcohol, when it is obtained in long, orange-coloured needles, melting at 182°, and soluble in ether with a green fluorescence:

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* Indican of 94 per cent. purity was here employed.

Found, N = 4·30. $C_{19}H_{15}O_5N$ requires N = 4·15 per cent.

Dihydroxybenzaldehydeindogenide gives with mordanted woollen cloth the following shades:

Chromium.	Aluminium.	Tin.	Iron.
Maroon	Dull scarlet	Orange	Deep blackish-brown

When calico mordanted with iron and aluminium is employed, rather poorer colours are produced, and the employment of calcium acetate or chalk in the dye-bath has a detrimental effect. The shades also were not quite fast to the action of soap. By digesting a mixture of indican * (2·5 grams), *p*-hydroxybenzaldehyde (2·5 grams), and oxalic acid (2 grams) in a little water for a short time at the boiling point, a semi-crystalline precipitate of p-*hydroxybenzaldehydeindogenide* separates. It was purified by a similar method to that employed with the preceding compound:

Found, N = 6·11. $C_{15}H_{11}O_2N$ requires N = 5·90 per cent.

This compound consists of orange-red needles, melting at about 267—269°, and dissolves sparingly in ether, giving a green, fluorescent solution. It is soluble in sodium hydroxide solution, with a dull scarlet coloration, but does not dye mordanted fabrics.

The *acetyl* derivative, $C_{15}H_{10}O_2N{\cdot}C_2H_3O$, is readily prepared in the usual manner, and forms bright orange leaflets, melting at 223—224°, which also dissolve in ether with a green fluorescence:

Found, N = 5·23. $C_{17}H_{13}O_3N$ requires N = 5·02 per cent.

In the previous communication (*loc. cit.*), it was pointed out that when a mixture of indican and nitrosodimethylaniline is dissolved in boiling acetic acid, the addition of a few drops of hydrochloric acid causes the separation of indigotin in beautiful glistening leaflets, the necessary oxygen being supplied by the nitrosodimethylaniline. It has been stated by Hazewinkel (*loc. cit.*) that acid oxidising agents convert indican into indigotin, but, on the other hand, a portion of the colouring matter is then further oxidised; it seemed possible, however, that by employing a milder oxidising agent than those hitherto used for this purpose, the secondary action might be avoided. The study of the behaviour of nitrosodimethylaniline in this respect was disappointing, and attempts to devise a quantitative process for the estimation of indican with this reagent have hitherto failed. As an instance, 0·125 gram of indican in 25 c.c. of water, treated with 0·5 gram of nitrosodimethylaniline in acetic acid, was digested with the addition of a few drops of sulphuric acid, by which means 0·045 of indigotin was obtained. Theory requires 0·0555 of indigotin, and it is likely that this and other poor results which have been obtained are due to the fact that it is necessary to carry on the operation at the boiling point in order to complete the reaction.

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* Purity 94 per cent.

The Hydrolysis of Indican with Acid, and Oxidation of the Solution by Means of Air.

By passing air through a hot solution of indican in dilute acid containing a little ferric chloride as an oxygen carrier, Hoogewerff and ter Meulen (*loc. cit.*) obtained 91 per cent. of the theoretical yield of indigo, but the purity of this product and the percentage of indirubin it contained was not then examined. Rawson again, in his interesting "*Report on the Cultivation and Manufacture of Indigo*" (Second edition, Calcutta, 1907), states that indigo was prepared in Java by Hazewinkel by hydrolysing the indican in the leaf extract by means of acid in the presence of an oxidising agent, and also describes a method, originated by himself, in which the necessary oxygen was supplied with ammonium persulphate, giving excellent results in the laboratory. As the quantitative aspect of this reaction, when air alone is employed as the oxidising agent, had not previously been studied with indican in this laboratory, and no published results have been found to exist in this respect with regard to the leaf extract, the matter was now investigated.

The acid indican solutions, contained in flasks surrounded by a water jacket carefully maintained at the required temperature, were oxidised by continuously aspirating air through the liquid. A separation of indigotin gradually took place, and at the conclusion of the experiment the product was collected, washed with 1 per cent. sodium hydroxide solution, dried, and weighed. To determine its purity, an aliquot portion was sulphonated, and the liquid diluted and titrated with titanium chloride, this reagent being employed for the analysis because of the presence of indirubin in the colouring matter. Experiment indicated that under the conditions given below, the reaction was almost complete

Time.	Indican.	Water.	Acid.	Temperature.	Indigotin.
80 minutes...	0·5 gram	1000 c.c.	4 c.c. H_2SO_4 *	60—90°	75 per cent.
150 ,, ...	0·5 ,,	—	—	—	84 ,,
195 ,, ...	0·5 ,,	—	—	—	85 ,,
8 hours......	0·501 gram	850 c.c.	—	60°	84·3 ,,
8 ,, ...	0·5 ,,	—	—	60	83·9 ,,

* (Pure), 96 per cent.

in two and a-half hours, was complete in three and a-quarter hours, and that a further digestion did not increase the yield.

It was thus evident that a quantitative yield of indigotin from indican could not be obtained under these conditions. The reason for this deficiency was partly explained by the fact that the acid filtrate from the indigotin was of a pale brown colour, and that the indigotin itself contained a small quantity of a brown compound, and was of but 93·8 per cent. purity as a rule. This brown compound is of a similar nature to indoxyl-brown, which, as previously shown (*loc. cit.*), is formed by the action of acids on indican in the absence of air, and is thus, it appears, formed even at the dilutions given above by means of the sulphuric acid. By employing half the quantity of sulphuric acid, that is, 2 c.c. in 850 of water, and oxidising for eight hours, it was found that the reaction was incomplete, and, moreover, that the supernatant liquid was markedly coloured, although not so strongly as was the case when the 4 c.c. of acid had been used. The presence of indirubin in moderate quantity in the colouring matter thus prepared is in accord with the statement of Beyerinck (*loc. cit.*), that in acid solutions indoxyl is oxidised very slowly by air, with production of much indigo-red, and at the same time part of the indoxyl is lost in another way. To account for the production of indirubin, it is only possible to consider that isatin is formed during the oxidation, and this point has been rendered certain by the isolation of isatin from a sample of Java indigo rich in indirubin (Proc., 1907, **23**, 30). Whether, as a rule, the whole of the isatin thus formed reacts with the indoxyl to form indirubin under the conditions of manufacture, or those given above, is not certain, and it is probable that a slight decrease in yield originates in this way. Rapid oxidation of indoxyl in acid solution, as with Rawson's persulphate process (*loc. cit.*), gave, on the other hand, a colouring matter, which, when examined, was found to be practically free from indirubin, and this further corroborates the work of Beyerinck.

Experiments were now carried out employing hydrochloric acid in the place of sulphuric acid at a concentration of 15 c.c. of the ordinary 33 per cent. pure acid (which is equivalent to the 4 c.c. of 96 per cent. sulphuric acid used previously) in 850 c.c. of water. The reaction proceeded very similarly to that described above, except that the indigotin separated in exceedingly minute crystals, and formed a beautiful coppery scum on the surface of the liquid. Under the microscope the product had the appearance of very minute, rather ill-defined, prismatic needles:

Time.	Indican.	Water.	Acid.	Temperature.	Indigotin.
8 hours	0·5	850	15 c.c.	60°	93·4 per cent.
8 ,,	0·5	850	15 ,,	60	93·5 ,,
9 ,,	0·5	850	15 ,,	70	87·6 ,,

These results were rather surprising, and indicate that hydrochloric acid gives in this respect much better results than sulphuric acid; this point does not appear to have been previously observed. The cause of this divergence was explained by the appearance of the acid filtrates from the indigotin, which were but very faintly yellow-coloured, and markedly differed in this respect from the corresponding sulphuric acid liquids. Some quantity of indirubin was also present in this colouring matter.

By means of the third experiment, it is shown that an increase of temperature is not beneficial, and this was again explained by the fact that the acid filtrate was more highly coloured than before. An experiment was now carried out with a freshly prepared extract of the leaves of *I. Sumatrana*, which, on analysis by the isatin method, gave indican (=0·04635 indigotin) in 100 c.c. Eight hundred and fifty c.c. of this liquid, together with 15 c.c. of hydrochloric acid, were heated to 60°, and air was then aspirated through the solution for nine hours. The precipitated colouring matter, which settled very readily, was collected, washed with dilute sodium hydroxide solution, weighed, and analysed as before by titanium chloride:

Found, indigotin = 0·3694. Theory requires 0·3939. Yield = 93·7 per cent.

The purity of the crude indigotin was 78·6 per cent.

This result is in close agreement with the experiments made on pure indican, although it should be noted that the concentration of the glucoside in the leaf extract was practically double that of the solutions of the pure substance above experimented with. There is little doubt that much larger amounts of indican could be effectively hydrolysed by this same volume of dilute hydrochloric acid.

At present, therefore, it has not been possible to obtain a theoretical yield of indigotin from indican, and it is to be noted that in this respect 93·5 per cent. is the highest amount as yet recorded in this laboratory.

Preliminary experiments on the behaviour of hydrochloric acid, and ferric chloride as an oxygen carrier, with indican solutions have indicated that there is little prospect of an increase of yield arising from an addition of the latter. Employing indican and acid in the concentrations given above, oxidising with air, and adding 0·1 gram of ferric chloride, the yield of indigotin produced after three hours and a-half at 60° was approximately 88 per cent.

Under the same conditions at 30°, the reaction was not completed in ten hours, and although the latter result is probably due to incomplete hydrolysis of indican, there is some reason to suspect that ferric chloride is not efficient as an oxygen carrier under the conditions which have been hitherto employed in this work.

Indoxyl-Browns.

In a former communication (Perkin and Bloxam, Trans., 1907, **91**, 279), the results of an examination of indigo-brown were given, and it was suggested that these compounds might have been produced from indoxyl during the process of manufacture. The fact that pure indican itself on digestion with acids gives a rather similar product (*loc. cit.*) supported to some extent this view, and especially so as indoxyl-brown, the main constituent of the mixture, possesses a percentage composition almost identical with one of the indigo-brown substances. A minor point of difference between these products was that the solution of indoxyl-brown in hot alcoholic potash possessed a green tint, but as more recent preparations of this substance have been devoid of this characteristic, it has been ascertained that this was not a property of the compound, but was due to its contamination with a minute trace of indigotin. The main distinction between indoxyl-brown and the indigo-brown constituent, however, consists in the fact that, whereas the former is insoluble in aqueous solutions of the alkali hydroxide, the latter dissolves, although only sparingly.

A further study of the action of acids on indican in the absence of an oxidising agent has been now carried out, with the desire of examining the more sparingly soluble product of the action referred to in the previous communication (*loc. cit.*), and to determine whether any distinction could be observed between the action of sulphuric acid originally employed and hydrochloric acid in this respect.

Two quantities of indican (2·5 grams in 100 c.c. of water) were respectively digested at the boiling point in the presence of carbon dioxide (A) with addition of 3 c.c. of sulphuric acid in 25 c.c. of water, and (B) with the equivalent of 33 per cent. hydrochloric acid for about two hours. The products were respectively diluted with 150 c.c. of water, and, when cold, the brown precipitates were collected and weighed:

Found, A = 1·1155 grams; B = 1·1190 grams.

The filtrates were of a pale orange-brown colour. These figures, as was previously found to be the case, are almost identical with that required by the amount of indoxyl, 1·127 grams, which the

2·5 grams of glucoside would yield on hydrolysis, being 98·9 and 99·3 per cent. of this weight. An examination of both products, as given below, indicated that they were practically identical. By extraction with boiling alcohol, a trace of indigotin remained undissolved, and by concentrating the solution, two substances could be isolated: (*a*) very sparingly soluble in alcohol, and (*b*) more readily so. An analysis of (*a*) gave N = 9·65 per cent., and this consisted of a dark reddish-brown powder easily dissolved by pyridine. Except as regards solubility in alcohol, it was almost indistinguishable from the substance (*b*) (found, N = 9·44), which consisted of the indoxyl-brown previously examined. The liquid from which the latter had been separated left on evaporation a pale brown, varnish-like residue, also insoluble in alkali. Found, N = 8·98 per cent.

Schunck and Römer (*Ber.*, 1879, **12**, 2311) have shown that their indican, when hydrolysed with cold acid in the absence of air, gave a product which, when treated with oxidising agents, did not form indigotin. This experiment was repeated in a somewhat similar way by treating 1·5 grams of pure indican, ground into a paste with 3 c.c. of water, with 5 c.c. of 33 per cent. hydrochloric acid, and keeping the mixture in an atmosphere of carbon dioxide for ninety hours. The solution soon became brown-coloured, and deposited a small quantity of a similar coloured precipitate, and this increased in quantity when the mixture was diluted with water. This product, which was readily soluble in alcohol, on treatment with ether gave a precipitate, found on examination to consist of indoxyl-brown, and the filtrate on evaporation yielded a brown, varnish-like residue very similar to that described above. Evidently, therefore, the action of cold acid for a long period on indican follows similar lines to that which takes place when the mixture is digested at the boiling point for a short time.

It has been shown (*loc. cit.*) that when boiling aqueous extracts of *I. Sumatrana* and *I. arrecta* are treated with acid, a brown precipitate is obtained, which represents in part the indican originally present. As regards the origin of indigo-brown, it appeared interesting to study this reaction quantitatively, especially in respect to the amount of nitrogen present in the brown matter.

Fifty grams of the leaves of *I. Sumatrana* (estimated by the isatin method to contain indican = indigotin 3·13 per cent.) were placed in a copper gauze cylinder, and extracted with water in a Soxhlet tube. The extract, evaporated to 100 c.c. approximately, was digested at the boiling point with an excess of hydrochloric acid, and after standing overnight the precipitate was collected and dried. It weighed 3·4775 grams, and was found to contain 6·51 per cent. of nitrogen, and thus represented 135·4 per cent. of the amount originally contained by the indican which was present.

In a second experiment, the leaf was extracted with methyl alcohol, the solution evaporated and treated with light petroleum, the precipitate dissolved in water, and the liquid freed from wax and chlorophyll by means of ether. One hundred c.c. of the aqueous liquid, containing 2·5 grams of indican, were digested at the boiling point for two hours with 3 c.c. of sulphuric acid, and after dilution with 150 c.c. of water and standing, the resulting precipitate was found to weigh 2·4110 grams. Analysis showed the presence of 6·74 per cent. of nitrogen, so that the amount contained by this product was 136·9 per cent. of that originally present in the 2·5 grams of indican. It is, of course, evident that as indoxyl-brown contains less nitrogen than indoxyl, the whole of the indican-nitrogen might not have been contained in these brown matters, but the experiments prove that in this sample of leaf a substance exists other than indican, which on digestion with acid gives, either alone or in the presence of indoxyl, a nitrogenous, brown precipitate.

It has been clearly proved by Rawson (*loc. cit.*) that the indigo-yielding property of the leaves on the living plant varies considerably; thus, for instance, plants the leaves of which gave in May 0·30 per cent. of indigotin, in August yielded 0·76, and in November only 0·25 per cent. Again, it is known that mere air-drying of the fresh leaf causes a decrease in the amount of indican, and an interesting decrease of the quantity of the glucoside in the air-dried leaf itself, on keeping, has been observed in this laboratory. Thus the sample employed in the above experiments, which were carried out approximately a year ago, was estimated then to give 3·13 per cent. of indigotin, whereas when recently analysed it was possessed of an indigotin value of only 2·45 per cent. No indigotin is formed as the result of this deterioration, and it seems likely that the point is to be explained by a change analogous to that which has been shown by Beyerinck to occur in woad leaves (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, **1**, 120), namely, that the action of excess of air on a dying woad leaf causes a loss of indoxyl with formation of unknown colourless and brown substances. In case such compounds formed by the deterioration of the indican were present in the leaf here employed and could be removed from the same by extraction with boiling water, it is evident that to obtain satisfactory information in the above respect an examination of the fresh leaf should be made at the period of its maximum indican content. A very interesting point in connexion with these experiments is that, whereas the indoxyl-browns given by pure indican are insoluble in alkali, the analogous plant preparations, although produced from solutions containing a similar concentration of the glucoside, are entirely dissolved in this manner. The only simple explanation of this phenomenon which suggests itself is that the leaf most probably contains, or its extract yields with acid, nitrogenous hydroxy-, aldehydic or ketonic substances, which condense with indoxyl or its alteration products to form the brown alkali soluble substance. The nature of a very large amount of the extractive matter of the leaf is unknown, but the pungent aromatic odour which is evolved when an extract is boiled with acid is somewhat in favour of this suggestion.

On the other hand, it seems certain, as a result of this investigation, that the indigo-brown obtained during the manufacture of natural indigo is not produced to any extent, if at all, by such a condensation of indoxyl with aldehydic or ketonic compounds derived from the plant. This theory, which at one time suggested itself as plausible, could not be maintained in view of the fact that when either pure indican, on the one hand, and the plant extract, on the other, are hydrolysed with hydrochloric acid, and the solutions simultaneously oxidised by air, the yields of colouring matter in both cases (94 per cent. approximately) bear an identical relationship to the indican originally present in each liquid. It is therefore evident that with the plant extract in these favourable circumstances, a secondary reaction of this character does not occur. In connexion with indigo-brown, however, it is interesting to note that all natural indigos appear to contain indigo-brown, so that this property is irrespective of their origin, which may have been due to such distinct plants as the *Indigoferae*, the *Polygonum tinctorium*, or the *Lonchocarpus cyanescens* of West Africa, and this point certainly favours the suggestion that indigo-brown is an indoxylic by-product of the manufacture, and represents a loss of colouring principle.

An examination of the leaves of the *Lonchocarpus cyanescens*, a plant which yields indigo and is used as a dye by the natives of Sierra Leone (*J. Soc. Chem. Ind.*, 1907, **26**, 389) under the name of the "Gara" plant, has been carried out with the object of isolating the colour principle. The air-dried material obtained for us with considerable trouble by Prof. Dunstan, of the Imperial Institute, to whom our best thanks are due, contained, unfortunately, no substance of this nature, and it was evident that a fermentation of the latter had ensued during the drying operation. It is thus probable that an investigation of the plant in this respect can only be carried out on the spot.

Our thanks are due to the India Office for a grant which has been partly employed during this work, and also to Sir Thomas Holderness for the active interest he has taken in this matter.

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XCI.—*Studies of Dynamic Isomerism. Part VIII. The Relationship between Absorption Spectra and Isomeric Change. Absorption Spectra of Halogen, Nitro-, and Methyl Derivatives of Camphor.*

By THOMAS MARTIN LOWRY and CECIL HENRY DESCH.

I.—*Introductory.*

IN the earlier papers of the present series a considerable number of cases of reversible isomeric change have been investigated by "dynamic" methods depending on observations of changes occurring in freshly-prepared solutions of one or other of the isomerides. The use of such methods is in practice confined to crystalline compounds, since only these can, as a rule, be separated in a pure form from mixtures of isomerides such as are normally produced in solution or in the liquid state. This limitation has the disadvantage of excluding some of the most important cases of dynamic isomerism, as, for instance, cyanic and hydrocyanic acids (Butleroff, *Annalen*, 1877, **189**, 77) and ethyl acetoacetate. Much information has been obtained by studying crystalline derivatives of these compounds, such as cyanocamphor, diethyl diacetylsuccinate (Knorr, *Annalen*, 1899, **306**, 332), or menthyl acetoacetate (Lapworth, Trans., 1902, **81**, 1499), but such observations can never entirely take the place of experiments on the original parent substances. Great importance attaches, therefore, to the discovery of "static" methods by which the presence of oscillatory isomeric changes may be detected *after the final balance has been attained*, and especially of methods that will also reveal the proportions in which the isomerides are present and the velocities with which they change from one form into the other.

Work on these lines has been undertaken by Perkin (Trans., 1892, **61**, 801), using magnetic rotatory powers as a test, and by Brühl (compare *Ber.*, 1902, **35**, 3510, 3619, 4030, 4113, etc.), who has made use of refractive indices; but compounds containing the group $\cdot CO\cdot CH_2\cdot CO\cdot$ usually possess abnormal optical properties (Kay and

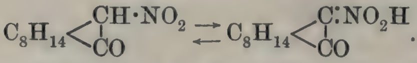
Perkin, Trans., 1906, **89**, 839; Brühl, Trans., 1907, **91**, 115) which seriously restrict the possibility of determining the proportions of ketone and enol, and lead in some instances to values, not intermediate, but entirely outside the values calculated for the two modifications (see, for instance, Brühl, *Ber.*, 1902, **35**, 4034). As these methods cannot in any case throw light on the velocities of the opposing isomeric changes, special interest attaches to the suggestion of Baly and Desch (Trans., 1904, **85**, 1029; 1905, **87**, 766) that a band in the ultra-violet absorption spectrum of a compound may not only indicate the occurrence of reversible isomeric change, but by its persistence may show the extent of the agitation hidden beneath the apparently placid behaviour of the substance.

This new view of the significance of absorption bands was based on a series of experiments with compounds containing the group

$$\cdot CO\cdot CH_2\cdot CO\cdot,$$

and was justified by the following observations. In contrast with ethyl acetoacetate, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot OEt$, which is generally regarded as almost wholly ketonic and gave no absorption band, acetylacetone, $CH_3\cdot CO\cdot CH_2\cdot CO\cdot CH_3$, a compound which Perkin had shown to be very largely enolised, gave a well-marked band. By adding an alkali, an equally strong band was developed in ethyl acetoacetate, but this could not be attributed to mere enolisation, since the enolic ethyl derivative, $CH_3\cdot C(OEt)\colon CH\cdot CO\cdot OEt$, in which the compound is completely locked up in this form, gave no absorption band whatever. As neither type of structure was capable of producing a band, its appearance in the spectra of the diketones and their metallic derivatives was attributed to an oscillation between the isomeric forms of these substances. Unfortunately, very little is known of the extent or velocity of isomeric change amongst the diketones, and it was therefore decided to make a series of observations of the absorption spectra of the simpler derivatives of camphor in the hope of establishing a quantitative relationship between their known velocities of isomeric change and the persistence of their absorption bands.

II.—*Nitro-compounds.*

Nitrocamphor, 
$C_8H_{14}<\begin{matrix}CH\cdot NO_2\\ |\\ CO\end{matrix} \rightleftarrows C_8H_{14}<\begin{matrix}C\colon NO_2H\\ |\\ CO\end{matrix}$.—Nitrocamphor, which had supplied the material for the earliest series of experiments on dynamic isomerism, was selected as the first substance for spectroscopic examination, since in this case information was already available, not only in reference to the extent of the change (Trans., 1904, **85**, 1541), but also as to its velocity in different solvents (Trans., 1899, **75**,

219; 1908, **93**, 110) and in presence of different agents by which the normal rate of change can be accelerated (Trans., 1908, **93**, 107) or retarded (*ibid.*, 119). As the period occupied by the change could be varied at will from a few seconds to a year or more, the conditions appeared to be particularly favourable for establishing a definite relationship between the velocity of the change and the persistence of the absorption band.

The solvents used were alcohol, ether, ethylene dichloride, and finally, ethylene dichloride to which a trace of acetyl chloride had been added in order completely to arrest the isomeric change. In spite of the wide range of velocities (roughly 10,000 to 1), no great alteration was seen in the form of the absorption curve. Each spectrum showed a "step-out" or rapid extension of the limit of transmission when the thickness was reduced to about 10 mm. of $N/100$ solution, but this did not disappear when isomeric change was practically stopped by the addition of acetyl chloride, and did not mature into a band when the period of change was reduced to a few hours by the use of alcohol as solvent.

Experiments on the use of alcohol and water as affording a more active solvent than pure alcohol had to be abandoned, as it was not practicable under the ordinary conditions of experiment to maintain the high standard of purity that was necessary. An alternative method of accelerating the change without converting the nitrocamphor into a salt was found, however, in the use of an acid catalyst (Trans., 1908, **93**, 116). For this purpose an alcoholic solution was made up to contain nitrocamphor $N/100$ and trichloroacetic acid $N/100$; its absorption curve showed a horizontal "step-out" as in the case of the neutral solutions, but no band was developed, and the catalytic action of the acid appeared to be entirely without influence on the form of the absorption curve.

It is clear, then, that the isomeric change of nitrocamphor, even although it involves the actual transference of a mobile hydrogen atom and takes place with a high velocity in both directions,* can proceed incessantly without resulting in the production of a band.

Alkali Salts of Nitrocamphor.

On the addition of alkali to the nitrocamphor solutions a very deep band was developed, extending down to a thickness of only a few mm. of $N/10,000$ solution, but only under such conditions that mutarotation experiments were quite out of the question. The band appeared, indeed, to be characteristic of the salts of nitrocamphor and not in any way of the nitro-compound itself, since on comparing solutions containing:

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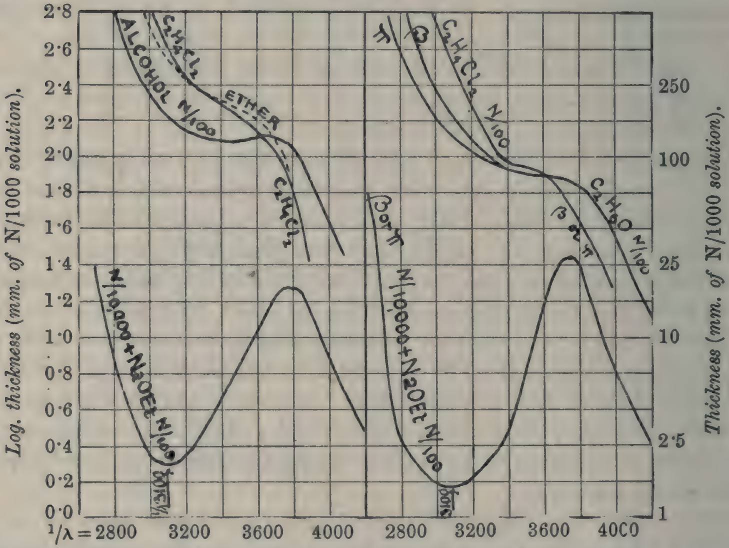
* The diketones change much less readily.

(*a*)	Nitrocamphor,	*N*/1000	Sodium ethoxide, *N*/10,000
(*b*)	,,	*N*/10,000	,, ,, *N*/10,000
(*c*)	,,	*N*/10,000	,, ,, *N*/100

no intensification of the band could be detected as a result of adding nine additional equivalents of nitrocamphor in (*a*), or ninety-nine equivalents of sodium ethoxide in (*c*). The latter result is in contrast with the behaviour of the diketones, which develop a maximum absorptive power only in presence of a large excess of alkali, but is in agreement with the known behaviour of nitrocamphor, as a strong acid which would be neutralised by a simple equivalent of alkali, forming salts which would not be hydrolysed in solution.

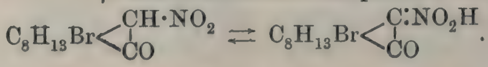
FIG. 1.

Nitro-derivatives of camphor.



Absorption curves for (a) *nitrocamphor;* (b) *β- and π-bromonitrocamphor in ethylene chloride, ether, and alcohol* N/100; *and for* N/10,000 *solutions of their sodium salts in alcohol.*

β- and π-*Bromonitrocamphors*,

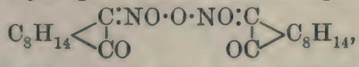


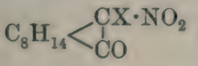
$$C_8H_{13}Br\Big<\begin{matrix}CH\cdot NO_2\\ | \\ CO\end{matrix} \rightleftharpoons C_8H_{13}Br\Big<\begin{matrix}C\colon NO_2H\\ | \\ CO\end{matrix}.$$

A preliminary test had shown that the mutarotation of nitrocamphor was not accompanied by any marked change in the form of the absorption curve, in spite of the fact that the composition of the solution changed from $\left\{\begin{matrix}\text{normal } N/100\\ \text{pseudo } \quad —\end{matrix}\right\}$ to $\left\{\begin{matrix}\text{normal } N/120\\ \text{pseudo } N/600\end{matrix}\right\}$. As the formation of an alkali salt could probably be detected at a concentration of $N/100,000$, it was evident that the absorptive power of the ψ-nitro-compound must have been something like one thousand times smaller than that of the salts derived from it.

In order to test this conclusion more closely, experiments were made with β- and π-bromonitrocamphors, the former of which crystallises out in the *normal* form, and when dissolved shows a change of rotatory power from left towards right, whilst the latter crystallises in the *pseudo*-form and shows a large change from right to left, owing to the conversion of five-sixths of the material into the normal form. Freshly prepared alcoholic solutions showed a somewhat greater transmission in the thicker layers by the *normal* β-compound than by the pseudo-π-compound, but the curves became identical lower down and were throughout of precisely similar type; freshly prepared solutions in ethylene dichloride gave identical curves of the same type as in the case of nitrocamphor. There is, therefore, evidently no special feature in the spectra of the ψ-nitro-compounds to mark them out from the normal modifications, and the band which is produced, not only by the salts of nitrocamphor, but in practically identical form by the salts of its β- and π-bromo-derivatives, must be attributed to some other cause than the presence of a ψ-nitro-structure.

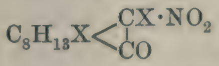
Derivatives of Nitrocamphor not Exhibiting Mutarotation.

Identical conclusions were arrived at from the study of derivatives in which the structure is fixed in the normal or in the pseudo-form by eliminating the mobile hydrogen atom. The compounds examined were the anhydride,  $C_8H_{14}<\begin{matrix}C{:}NO{\cdot}O{\cdot}NO{:}C\\ | \qquad\qquad\qquad | \\ CO \qquad\qquad\qquad OC\end{matrix}>C_8H_{14}$, of ψ-nitrocamphor, and several halogen derivatives of the normal type,



$$C_8H_{14}<\begin{matrix}CX{\cdot}NO_2\\ | \\ CO\end{matrix}$$

and



$$C_8H_{13}X<\begin{matrix}CX{\cdot}NO_2\\ | \\ CO\end{matrix}$$

(X = Cl or Br).

The curves for the anhydride and for the two stereoisomeric aa'-chloronitrocamphors showed a somewhat rapid extension between 25 and 8 mm. of $N/100$-solution; the aa'-bromonitro-compound gave an almost linear curve. In no case did the curves show a band* or other special feature, and it is therefore obvious that neither the normal nor the pseudo-type of structure is capable *per se* of generating an absorption band.

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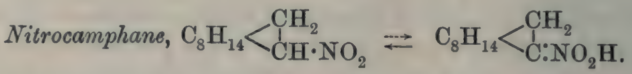
* A band was produced by the chlorobromonitrocamphor formed as a by-product in attempting to purify crude πa-chlorobromocamphor with nitric acid (Trans., 1906, **89**, 1041), but no importance can be attached to this until the constitution of the compound has been established by reduction and other methods.



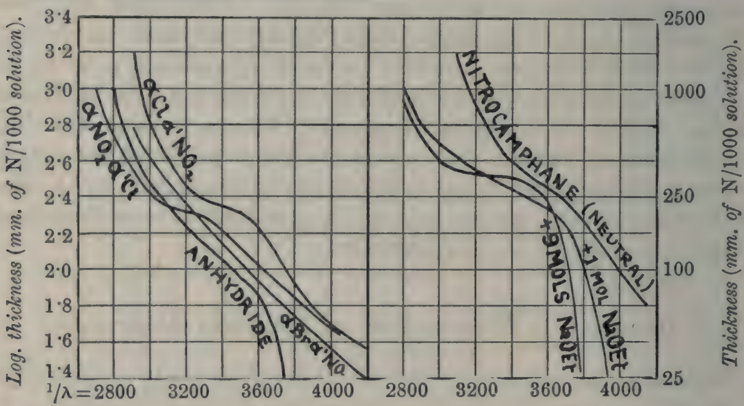
$$\textit{Nitrocamphane},\ C_8H_{14}<\begin{matrix}CH_2\\|\\CH\cdot NO_2\end{matrix} \rightleftarrows C_8H_{14}<\begin{matrix}CH_2\\|\\C{:}NO_2H.\end{matrix}$$

By the kindness of Dr. Forster, who supplied us with a considerable quantity of material, we were able to compare the behaviour of nitrocamphane with that of nitrocamphor. The chief differences that result from the elimination of the ketonic group are:

(*a*) A displacement of the equilibrium, so that the normal compound exhibits a constant rotatory power in solution, whilst the labile pseudo-compound passes over completely into the normal form.

FIG. 2.

(1) "*Fixed*" *derivatives of nitrocamphor,—anhydride, αα′-chloronitrocamphors* (2), *and αα′-bromonitrocamphor;* (2) *Nitrocamphane, alone and with* 1 *and* 9 *equivalents of alkali; in centinormal alcoholic solutions.*

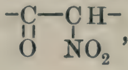


(*b*) A weakening of the acid properties of the substance, so that neutral salts no longer exert an accelerating action on the isomeric change; as a consequence, the pseudo-compound can be isolated by merely acidifying an aqueous solution of its salts.

Spectroscopic observations showed the existence of a slight extension in the absorption curves of nitrocamphane and of freshly prepared solutions of the labile ψ-isomeride, but this was even less pronounced than in the case of nitrocamphor, and only of about the same order of magnitude as in the "fixed" ψ-anhydride and normal chloro-derivatives. Moreover, in marked contrast with the behaviour of nitrocamphor, the addition of an equivalent of sodium ethoxide does not give rise to a band, and even nine equivalents do no more than bring the "step-out" to a horizontal position, as in neutral solutions of nitrocamphor. It appears, therefore, that in this simpler nitro-compound isomeric change gives rise to no absorption band either in the parent substance or in its alkali salts.

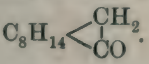
Results which have been obtained elsewhere since these experiments were commenced support this view. Thus Hedley (*Ber.*, 1908, **41**, 1195) found that simple nitro-compounds, even when in the ψ-nitro-form, as in solutions of their salts, did not give an absorption band, but that the presence of a second nitro-group was necessary in order that a band might be developed. Baly and Desch (Trans., 1908, **93**, 1749) found, contrary to Hedley's statement, that a small but distinct band was given by nitromethane and nitroethane. The behaviour of this band in alkaline solutions was, however, somewhat anomalous, and apart from this instance, it was found that conjugation of the nitro-group with an ethylenic linking, as in ω-nitrostyrene,

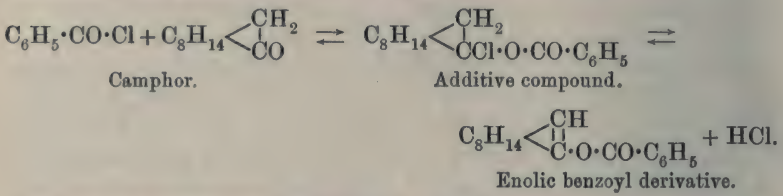
$$C_6H_5{\cdot}CH{:}CH{\cdot}NO_2,$$

or with a group possessing residual affinity, as in methylnitroamide, $CH_3{\cdot}NH{\cdot}NO_2$, was necessary to produce a band. In nitrocamphor, the neighbourhood of the carbonyl group,  $-\underset{\underset{O}{\|}}{C}-\underset{\underset{NO_2}{|}}{C}H-$, provides the required conjugation.

III.—*Halogen Derivatives.*

In view of the negative character of the results described above, it was decided to enlarge the scope of the research and to include all the simpler derivatives of camphor which had been investigated in previous papers of the series, together with a number of other compounds, the examination of which might throw light on the conditions under which an ultra-violet absorption band might be produced. The general result was to show that, not only may isomeric changes occur in the case of the nitro-compounds without any development of a band, but conversely amongst the halogen derivatives bands may be developed by compounds or under conditions such that all possibility of isomeric change was excluded. In order to make this clear, it will be convenient, before describing the spectroscopic observations, to summarise the information that is available in reference to isomeric changes in this series of compounds.

So far as the parent substance is concerned, it is generally recognised that the properties of camphor are those of the cyclic ketone,  $C_8H_{14}<\begin{matrix}CH_2\\|\\CO\end{matrix}$. To this view no exception can be taken on the ground that it yields an enolic benzoyl derivative when boiled with benzoyl chloride (Lees, Trans., 1903, **83**, 152), since this may result from the formation and decomposition of an intermediate compound without involving the formation of any trace of enolic camphor:



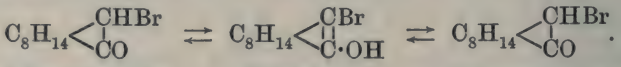
$$\mathrm{C_6H_5\cdot CO\cdot Cl + C_8H_{14}}<\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CO}\end{matrix} \rightleftharpoons \mathrm{C_8H_{14}}<\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CCl\cdot O\cdot CO\cdot C_6H_5}\end{matrix} \rightleftharpoons \mathrm{C_8H_{14}}<\begin{matrix}\mathrm{CH}\\ \|\\ \mathrm{C\cdot O\cdot CO\cdot C_6H_5}\end{matrix} + \mathrm{HCl}.$$

Camphor. Additive compound.

Enolic benzoyl derivative.

Camphor itself is, however, not an ideal substance on which to investigate isomeric change, since its crystallisation from solution is unsatisfactory and its solubility excessive. The β-bromo-derivative, $\mathrm{C_8H_{13}Br}<\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CO}\end{matrix}$, has the advantage of excellent crystalline properties and a smaller solubility, whilst retaining most of the characteristic properties of the parent substance. Careful observations, including a number of tests carried out specially for the purpose of the present investigation, have failed to reveal any changes of rotatory power in the freshly prepared alcoholic solutions, and it has already been shown (Trans., 1906, **89**, 1037) that no increase of solubility results from the addition of a trace of alkali to the saturated solution. Enolisation, if it takes place at all, must therefore be limited to a very small proportion of the material in solution.

In the case of α-bromocamphor the evidence is much more decisive, owing to the fact that the keto-enolic change is associated with possibilities of stereoisomerism, the hydrogen atom of the enol reverting either to the α- or to the α′-position in the ketone:



$$\mathrm{C_8H_{14}}<\begin{matrix}\mathrm{CHBr}\\ |\\ \mathrm{CO}\end{matrix} \rightleftharpoons \mathrm{C_8H_{14}}<\begin{matrix}\mathrm{CBr}\\ \|\\ \mathrm{C\cdot OH}\end{matrix} \rightleftharpoons \mathrm{C_8H_{14}}<\begin{matrix}\mathrm{CHBr}\\ |\\ \mathrm{CO}\end{matrix}.$$

α-Bromocamphor. Enolic form. α′-Bromocamphor.

This change has been shown by Kipping (Proc., 1905, **21**, 125) to take place in alkaline, but not in neutral or acid, solutions; in spite of the fact that only about 6 per cent. of the α′-compound is formed, it is accompanied by a decrease of rotatory power from $[\alpha]_D$ 135° to 122°, which renders it very easy to detect by polarimetric observations. It is important to notice that the proportion of enol affects the velocity, but not the extent, of the alteration of rotatory power; it is therefore possible, by extending the observations over a considerable period, to detect the formation of the most minute quantities of the enolic form. The advantage gained by this method of procedure is such that, whilst observations of rotatory power might detect the formation of 1 per cent. of enol from β-bromocamphor, in the case of the α-compound the corresponding proportion would be more like one part in a million, and this minute proportion may be taken as an upper limit of the amount of enolisation in neutral solutions of α-bromocamphor.

Similar statements may be made in reference to all the halogen derivatives of camphor which contain the group ·CHX·CO·, since these are all completely stable in neutral solutions, but undergo stereoisomeric change when enolisation is induced by the addition of a trace of alkali. If, therefore, the appearance of an absorption band were directly related to the occurrence of reversible isomeric change, such a band should appear (as in the case of nitrocamphor) only on the addition of alkali, and not, as is actually the case, indifferently in neutral and alkaline solutions.

Derivatives containing the group $\cdot CH_2\cdot CO\cdot$ or ·CXY·CO· show no change of rotatory power or of solubility on the addition of alkali. In the former case it may reasonably be assumed that compounds, such as camphor or β-bromocamphor, behave in essentially the same way as α-bromocamphor, that is, that they are enolised by the addition of alkali, although to so small an extent that, in the absence of a further stereoisomeric change no alteration can be detected in the properties of the solution. The disubstituted compounds, on the other hand, from which both α-hydrogen atoms have been displaced are presumably exempt from all possibility of enolisation.

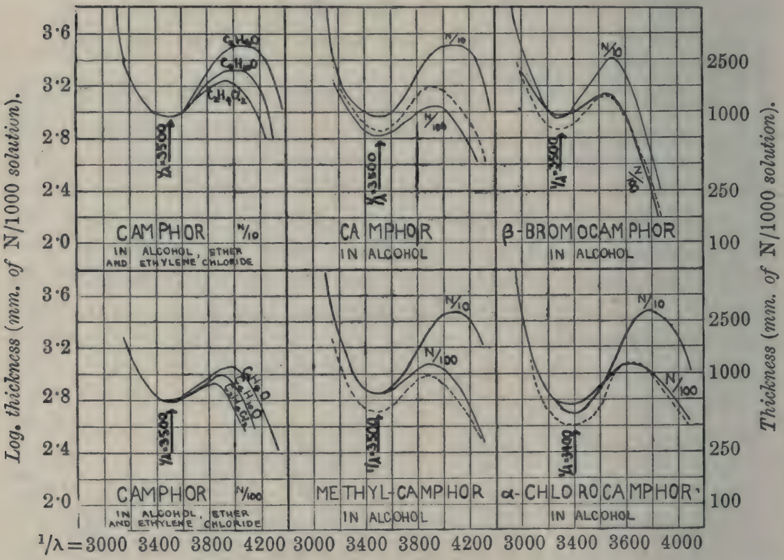
The Absorption Spectrum of Camphor.

The absorption spectrum of a N/100-solution of camphor in alcohol was examined as long ago as 1881 by Hartley (Trans., **39**, 153), who reported that the pure substance was remarkably diactinic and showed no absorption band. Baly, Marsden, and Stewart (Trans., 1906, **89**, 979), working with more concentrated solutions, found an absorption band persisting over a range of thickness of about 10 to 1, and this has since been confirmed by Hartley (Proc., 1908, **24**, 120). As our sliding-tube permitted of observations being made with thicknesses of solution up to 250 mm., we have been able to investigate the band in *N*/100- as well as in *N*/10-solutions. The *N*/100-solutions we have found, in confirmation of Hartley's observations, to be diactinic up to thicknesses of 60 mm., but at greater thicknesses a shallow band is observed ; in neutral solutions the band persists over 2 or 3 exposures only, but the addition of an equivalent of alkali extends the range to 3 or 4 exposures, each representing a change of thickness in the ratio 1·26 to 1.

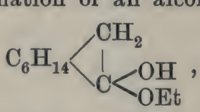
Our curve for the *N*/10-solutions is very similar to that recorded by Baly, Marsden, and Stewart, but the band was found to extend over six instead of ten exposures. This difference is probably due to the fact that the upper part of Baly's curve was plotted from observations made with $N/1$-solutions. As camphor does not obey Beer's law, the absorption produced by a millimetre of $N/1$-solution would not be the same as that produced by a centimetre of $N/10$- or a decimetre of $N/100$-solution, and the use of the stronger solution would inevitably lead to a further intensification of the band.

It was at first thought that the weakening of the camphor band which results from diluting the solution from $N/1$ to $N/100$ strength might be due to the formation of an alcoholate,

FIG. 3.



Absorption curves showing influence of solvent and concentration. The dotted curves show the effect of an equivalent of sodium ethoxide added to the N/100*-solutions.*



$$C_6H_{14}\langle \begin{matrix} CH_2 \\ | \\ C < \begin{matrix} OH \\ OEt \end{matrix} \end{matrix},$$

in presence of the larger excess of alcohol. This view was negatived by observations which showed a precisely similar change in ether and in ethylene dichloride. Another possibility, that the band might be due to polymerisation of the ketone, was rendered improbable, although not altogether disproved, by the fact that the bands were progressively weaker in alcohol, ether, and ethylene dichloride, although the latter solvents usually permit a higher degree of association than alcohol.

Mono-derivatives of Camphor.

Precisely similar changes were observed in the absorption spectrum of α-methylcamphor on diluting the alcoholic solution from *N*/10 to *N*/100 and on adding an equivalent of alkali to the *N*/100-solution, the curves in each case being almost identical with those for the parent substance. The three curves for β-bromocamphor differed only in that the persistence of the bands was one unit less throughout, whilst those for α-bromocamphor (which could only be plotted for *N*/100-solutions) were a unit stronger and showed a shifting of the head of the band from 1/λ 3500 to 1/λ 3350. The three curves for α-chlorocamphor also showed an intensification of the camphor band, resulting from the introduction of the α-halogen atom, the head of the band being shifted at the same time from 1/λ 3500 to 1/λ 3400. *N*/100-solutions of the αβ- and απ-dihalogen derivatives gave bands of the same persistence as in the case of camphor, the intensification due to the α-halogen atom being balanced by the repressive action of the bromine in the β- or π-position, and showed the same slight intensification on the addition of an equivalent of alkali.

The change of persistence which results from the addition of alkali, although generally observed amongst the simpler derivatives of camphor, gives no representation whatever of the effect which the alkali produces on the velocity of isomeric change. In neutral solutions the change is infinitely slow; on the addition of an equivalent of alkali, it is practically instantaneous,* but the effect on the absorption curve is so insignificant that it will not even bear comparison with the change produced by merely altering the concentration of the alcoholic solution. Evidently, therefore, the presence of the band cannot be correlated, even in a qualitative way, with the occurrence of isomeric change in this series of compounds.

αα′-Di-derivatives of Camphor.

It has already been mentioned that when the α′-hydrogen atom of α-bromocamphor is displaced by a nitro-group, the resulting α-bromo-α′-nitrocamphor gives no absorption band, but an almost linear absorption curve. The band of α-chlorocamphor, on the other hand, although destroyed by nitration, leaves behind in the α-chloro-α′-nitro-compound an extension of the spectrum at the same oscillation-frequency and almost at the same thickness of solution as the head of the chlorocamphor band; there can, therefore, be little doubt that the extension represents an early stage in the development of the band. On account of the greater amount of material that was available, the idea suggested by this observation was worked out with α-bromocamphor, the α′-hydrogen atom of which was displaced by the radicles $\cdot NO_2$, $\cdot CHO$, $\cdot Br$, $\cdot CH_2Br$, $\cdot Cl$, and $\cdot CH_3$. The bromonitro-compound proved to be an exceptional limiting case, all the other members of the series giving strongly inflected curves. Thus the bromoformyl and dibromo-compounds showed an extension almost as pronounced as in the extreme curve for nitrocamphor; in the next two members of the series, the extension was so rapid that the curves were brought right up to a horizontal position, and could be represented most accurately by showing the presence of a slight minimum; finally, in the case of the α-bromo-α′-methylcamphor, the absorption curve showed an unmistakable band persisting over two exposures.

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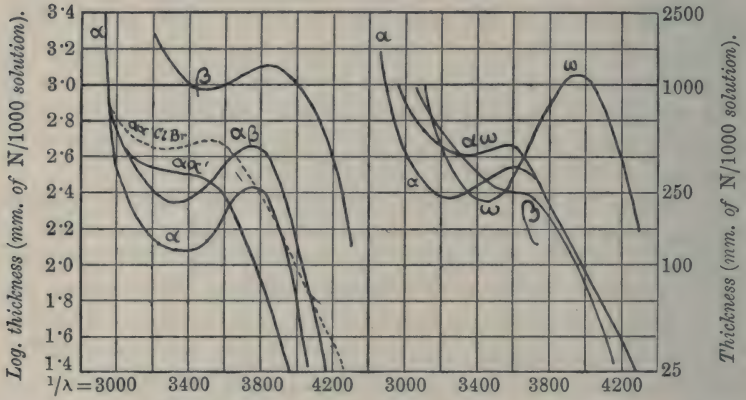
* The addition of one thousandth of an equivalent of sodium ethoxide to a normal solution of α-bromocamphor is sufficient to establish a condition of equilibrium within an hour; the proportional period for one equivalent would be about three seconds.

FIG. 4.

Bromo-derivatives of (1) *Camphor;* (2) *Methylcamphor.*



Absorption curves for N/100-*solutions in alcohol. Notice the gradual disappearance of the band in the series* (1) *α-bromo-, αβ-dibromo-, β-bromo-, α-chloro-α′-bromo-, and αα′-dibromo-camphor;* (2) *ω-bromo-, α-bromo-, αω-dibromo-, β-bromo-methyl-camphor.*

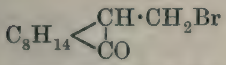
From these observations it is clear:

(1) That no sharp line of demarcation can be drawn between compounds which show an absorption band and those that do not, and

(2) That a definite band may be produced by a compound in which all possibility of keto-enolic change has been removed by the displacement of the whole of the mobile hydrogen.

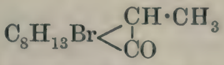
Isomeric Bromomethylcamphors.

If further evidence were needed to show that isomeric change is not the main factor in determining the appearance of the absorption band, it is provided in a particularly striking form by a comparison of the three isomeric bromomethylcamphors supplied to us by Dr. Glover:



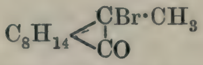
$C_8H_{14}<\begin{array}{l}CH\cdot CH_2Br\\ CO\end{array}$

ω-Bromomethylcamphor.



$C_8H_{13}Br<\begin{array}{l}CH\cdot CH_3\\ CO\end{array}$

β-Bromomethylcamphor.



$C_8H_{14}<\begin{array}{l}CBr\cdot CH_3\\ CO\end{array}$

α-Bromomethylcamphor.

Of these three compounds the first two are free to undergo keto-enolic change, whilst the last is fixed by the elimination of the α- and α′-hydrogen atoms. The absorption curve for the ω-bromo-compound showed the deepest band that we have observed amongst the halogen derivatives of camphor, the persistence in $N/100$-alcoholic solutions being six exposures as compared with four for α-bromocamphor, three for camphor and methylcamphor, and two for β-bromocamphor; the bromine in this position evidently exerts a maximum effect, possibly on account of the leverage which it acquires from the interposition of the methylene group. A comparison of the α- and β-compounds showed that, whilst the former, as has already been mentioned, gives a shallow band, the latter merely gives a well-marked horizontal extension. This result is directly opposed to what might have been anticipated from the fixity of the α-compound and the mobility of the β-isomeride, but is fully in accord with the general tendency disclosed by the observations which have shown that the absorption band of camphor is strengthened by an α-bromine atom, but weakened by a bromine atom in the β-position; if this tendency be regarded as dominant in the case of methylcamphor, the observations now recorded are abnormal only in the average weakness of the band in these two bromo-derivatives.

IV.—*Origin of the Absorption Bands.*

Whilst it would obviously be premature to attempt to construct, from observations of a limited group of compounds, a general theory as to the origin of absorption bands, certain conclusions derived from the present investigation may usefully be stated as affording data from which a complete theory may at some future date be developed.

It is evident that the original suggestion, referred to at the beginning of this paper, that the absorption band observed amongst ketonic compounds is associated with the transfer of a labile hydrogen atom and that its persistence is a measure of the number of molecules in the solution that are actually undergoing isomeric change, cannot be maintained, as had, indeed, already become probable from the evidence accumulated by Baly and his co-workers. The facts which tell most strongly against this view are:

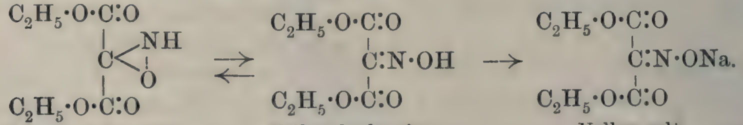
1. The reversible isomeric change of nitrocamphor and of nitrocamphane, the occurrence of which is clearly demonstrated by independent methods, does not cause selective absorption, although the alkali salt of ψ-nitrocamphor gives rise to a very strong absorption band.

2. In the simpler derivatives of camphor, the band is produced with equal facility whether the substance is undergoing isomeric change or not, and a weak band may even be produced by those derivatives in which isomeric change is impossible, owing to the complete displacement of the labile hydrogen atoms.

In the present investigation we are concerned with absorption bands of two types which must be carefully distinguished from one another, namely, (1) the bands which are produced by the alkali salts of nitrocamphor and of its β- and π-bromo-derivatives, but not by the parent substances or their "fixed" derivatives, and (2) the bands which are developed by the majority of the simpler derivatives of camphor in neutral and alkaline solutions indifferently.

Origin of the Nitrocamphor Band.—In the case of nitrocamphor our observations show clearly that neither the normal nitro-compound nor its ψ-nitro-isomeride gives rise to an absorption band, which first appears when the hydrogen atom of the ψ-nitro-group is displaced by an alkali metal. The view that the ionisation of the salt is the effective cause of its remarkable absorptive power is supported by few, if any, analogous cases, and by no direct experimental evidence. On the contrary, it has become a universal custom, when the band falls within the limits of the visible spectrum, to attribute the development of colour during neutralisation to a change of structure, as in the case of phenolphthalein or p-nitrophenol, and it is difficult to avoid the conclusion that some similar change takes place during the neutralisation of nitrocamphor.

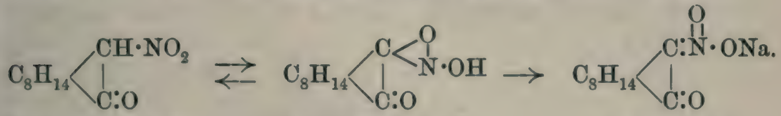
This view is rendered exceedingly probable by the analogous behaviour of the *iso*nitroso-derivatives of malonic acid studied by Dr. Whiteley (Trans., 1903, **83**, 34). These exist in colourless (*iso*-oxime) and in coloured (hydroxime) modifications, but invariably give rise to coloured (hydroxime) salts:



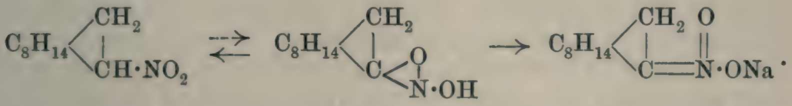
Colourless *iso*-oxime. Yellow hydroxime. Yellow salt.

In the case of nitrocamphor the possibility of two alternative formulæ for the ψ-modification has long been recognised and discussed

(Lowry, Trans., 1898, **73**, 995; Forster, Trans., 1900, **77**, 254; Perkin, Trans., 1902, **81**, 304). There is therefore nothing inherently improbable in the suggestion that the conversion of ψ-nitrocamphor into its salts is accompanied by a change of structure, in which the nitrogen atom passes from a tervalent to a quinquevalent condition:


Normal nitrocamphor. ψ-Nitrocamphor. Sodium salt.

It will be noticed that the formula for the sodium salt contains a series of conjugated double bonds which is lacking, not only in both forms of the parent substance, but in all three modifications of nitrocamphane:



The explanation now suggested is, therefore, entirely in accord with our own observations, as well as with those of the other workers referred to above (p. 813).

Origin of the Camphor Band.—The weaker absorption band developed by camphor and its simple halogen and methyl derivatives requires a different explanation, and at the present time constitutes a more difficult problem than that of the nitrocamphor band discussed above.

As borneol produces no selective absorption, the camphor band is evidently in some way a function of the ketonic group, but it is not at all easy to say in what way the group acts in promoting the formation of the band. So far as the chemical properties of the group are concerned, it must be recognised that the appearance of the band is not related in any direct way to the property possessed by some members of the series of undergoing keto-enolic isomeric change. Nor have we succeeded as yet in associating the band with the polymerisation of the molecule. Finally, the intensity of the band cannot be correlated with the "reactivity" of the carbonyl group towards agents such as hydroxylamine, since α-chlorocamphor and α-bromocamphor, which do not yield oximes, give deeper bands than camphor, methylcamphor, and β-bromocamphor, which readily react with this agent.

On the physical side, however, the gradual strengthening or weakening of the absorptive power of the molecule by various substituents, and especially by those which are contiguous to the carbonyl group, suggests a close analogy with other optical properties, such as refractive power and magnetic rotation, which are particularly sensitive to the influence of contiguous or conjugated groups. At present, therefore, the most hopeful method of attacking the problem consists in studying the relationship between the absorption and the other optical properties of the various compounds. Work on these lines is already in progress, and it is anticipated that the results will prove to be of value in elucidating the various factors which regulate the power of selective absorption possessed by the various compounds of the camphor group.

V.—*Methods of Observation.*

The methods used were essentially the same as those described by Baly and Desch (*loc. cit.*), and need not be set out in detail. The earlier observations were made on a "No. 2" spectroscope by Hilger, with a single pair of quartz half-prisms and fully-achromatised quartz-calcite lenses of 13″ focus. The photographs were taken with a half-plate camera provided with a graduated swing-back and a partly-achromatised quartz-calcite lens of 22″ focus moving in a graduated tube. This gave a spectrum about 10 cm. long, and twenty-four exposures could be made on a half-plate placed vertically in the camera.

In the later experiments two pairs of quartz half-prisms were used. This not only gave a much greater dispersion, but had the advantage of bringing the whole of the ultra-violet spectrum sharply into focus on a flat plate. With the new arrangement it was necessary to arrange the half-plate horizontally, but by using a slightly shorter slit it was still possible to make twenty exposures on each plate. At the same time it became necessary to exclude from the plate the greater part of the visible spectrum, but as none of the substances dealt with possessed any visible colour, this did not involve the loss of any part of the absorption; on the contrary, the useful part of the spectrum from λ 4100 to λ 2100 was spread out to the fullest advantage over a distance of 15 cm. right across the plate. The increased dispersion thus secured was found to be of the utmost value when dealing with substances which gave only shallow bands of slight persistence.

The solutions under observation were placed in sliding-tubes of the type devised by Baly, but instead of using a millimetre scale, a direct logarithmic scale of thicknesses was provided. The tube was about 300 mm. long, and the graduations were as follows:

Mm..........	251·2	199·5	158·5	125·9	100·0	79·4	63·2	50·1	39·8	31·6
Logs.........	2·4	2·3	2·2	2·1	2·0	1·9	1·8	1·7	1·6	1·5

Mm..........	25·1	20·0	15·9	12·6	10·0	7·9	6·3	5·0	4·0	3·2	2·5
Logs.........	1·4	1·3	1·2	1·1	1·0	0·9	0·8	0·7	0·6	0·5	0·4

These divisions were numbered consecutively from 21 to 1, and as the dark slide was also graduated and numbered to correspond with the tube, the risk of errors due to exposing a wrong thickness of solution was reduced to a minimum. Moreover, as each thickness exposed was made to correspond with a definite position of the plate, it was not necessary to make any record of the conditions of the observations except to note on the negative the nature and concentration of the absorbing solution.

The logarithmic method of graduation has the advantage that successive exposures represent exactly equal increments or decrements of concentration. A change of thickness in the ratio 10 to 1 is effected in 10 equal stages, each of which, by a happy coincidence, is almost exactly 5 to 4 (really 1·259 to 1); by a further coincidence the majority of the thicknesses approximate closely to round numbers of millimetres. One of the chief advantages of the logarithmic scale of thicknesses arises, however, from the fact that when the absorption curves are plotted (log-thickness against oscillation-frequency), the experimental points are equally spaced on the vertical axis and fall exactly on the main divisions of the curve paper. The appearance of the negative therefore approximates somewhat closely to the actual form of the absorption curve, the only deviation being due to the fact that, on the negative, the scale of oscillation-frequencies becomes more and more open on passing from the visible to the far ultra-violet.

The materials used were for the most part those which had been specially purified for experiments on mutarotation and solubility, and need not be further described. We are, however, indebted to Dr. M. O. Forster for the specimen of nitrocamphane used in the experiments and to Dr. W. H. Glover for the methyl derivatives of camphor, and desire to take this opportunity of expressing our thanks. The alcohol used was Kahlbaum's "absolute," distilled from a small amount of phosphoric oxide in order to remove all traces of basic impurity. The ether, "distilled from sodium," was redistilled from phosphoric oxide before being used. The ethylene dichloride was purified as described by Perkin (Trans., 1902, **81**, 308).

We desire to place on record our indebtedness to the Research Fund Committee of the Chemical Society for a grant which defrayed a portion of the cost of the investigation, to Prof. Armstrong and to Mr. E. C. C. Baly for valuable criticisms and advice, and to Mr. H. W. Southgate for assistance in the photographic work.

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XCII.—*Indican. Part III.*

By Frederick Thomas, William Popplewell Bloxam, and Arthur George Perkin.

In the preceding investigation (this vol., p. 793), an account has been given of the hydrolysis of indican by means of acids, and the present paper deals with the still more important question of the behaviour of the glucoside with its specific enzyme, indimulsin. With the exception of some preliminary experiments by Gaunt, Thomas, and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 1174), and the work of ter Meulen (*Rec. trav. chim.*, 1905, **24**, 444), no study has been made of the quantitative aspect of the hydrolysis of pure indican by the enzyme.

The discovery and characterisation of the indican enzyme is due to the elaborate investigations of the Dutch chemists, Hazewinkel, Beyerinck, and van Romburgh, as is also much of the work in connexion with the action of bacteria on infusions of certain indigo-yielding plants. Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, **1**, 120), after reference to earlier work which rendered the existence of such an enzyme probable, was the first to announce its discovery. The process consists of extracting the leaves of the plant in a fine state of division, first with cold 96 per cent. and subsequently with more dilute alcohol, which removes chlorophyll, indican, wax, etc., and leaves a snow-white, highly active powder. From such preparations of the leaves of *Polygonum tinctorium* and certain species of *Indigoferae*, the enzyme itself could be but imperfectly removed, for in water it is almost insoluble, only sparingly so in glycerol, and rather more readily in 10 per cent. solutions of sodium and calcium chlorides respectively. The residue which remains after extraction in this way was not perceptibly less active than before treatment, and in a subsequent communication (*ibid.*, 1900, **2**, 120) the insoluble character of the enzyme was confirmed. A minute study of these leaf preparations was carried out by Beyerinck in regard to their behaviour with partly purified indican solutions, as pure indican itself had not then been isolated, and he illustrates the effect of temperature on the intensity of the hydrolysis by means of curves. Among numerous points of interest, it was observed that ammonia quickly destroys the enzyme, and also that emulsin slowly hydrolyses indican, although the intensity of its action was only one-twentieth of that of *Indigofera* enzyme preparations. Certain other details of this work are alluded to in connexion with the experiments described below.

Hazewinkel, who investigated the subject in 1898, but did not publish his work until later (*ibid.*, 1900, **2**, 512), obtained independently results of a similar nature to those of Beyerinck. By means of his enzyme preparation, which he describes as being perfectly white, he proved for the first time that indican is a glucoside of indoxyl. Finding that emulsin also acted on indican solutions, he called the indican enzyme "indimulsin," and considered that a 10 per cent. solution of sodium chloride is the best medium for dissolving the latter.. A very interesting point which he mentions is that during fermentation no indican passes from the leaf into the surrounding liquid, a fact which he demonstrates in a very simple manner.

The paper of van Romburgh (*ibid.*, 1899, **2**, 344) contains results practically identical with those described above. Allusion is also made to the insoluble character of the enzyme, and to the activity of emulsin with solutions of indican.

Finally, Beyerinck (*ibid.*, 1900, **3**, 101) demonstrated that the ferment present in woad, *Isatis tinctoria*, is not an indican enzyme, and is not capable of hydrolysing this glucoside. It reacts, however, with isatan, the peculiar indigotin-yielding principle of this plant.

On the other hand, Bergtheil, without reference to the papers above discussed, states (Proc., 1904, **20**, 139) that "the fermentation of the indigo plant has been ascribed to a bacterium and also to enzymes, but has never been satisfactorily investigated," and that "the author shows that there are many bacteria capable of producing the fermentation, but it is, in the main, due to a specific enzyme occurring in the plant cells." Again, in the "*Report on the Cultivation and Manufacture of Indigo*" (Rawson, 2nd edition, Calcutta, 1907, p. 32), revised both by Rawson and Bergtheil, the statement occurs, ". . . the opinion was expressed that the active fermentation . . . was brought about by enzymes?" "This . . . has since been confirmed by much detailed work conducted by Mr. C. Bergtheil." It thus appears that the claims of the latter author are still maintained.

In many respects Bergtheil's paper (Trans., 1904, **85**, 877) covers ground already traversed by the Dutch chemists, Hazewinkel, Beyerinck, and van Romburgh, and has already been discussed to some extent by Gaunt, Thomas, and Bloxam (*loc. cit.*). It is referred to again later in this investigation, mainly in connexion with experiments on the solubility of the enzyme.

On the latter point, ter Meulen (*loc. cit.*) is in agreement with the other Dutch work referred to above, as is evident from his statement (p. 470), "L'enzyme de l'indigo est insoluble dans l'eau."

EXPERIMENTAL.

In the following fermentation experiments the enzyme was employed in the form o the purified leaf powder, and was prepared according to the directions of Beyerinck. Such a procedure was adopted as being somewhat akin to the factory conditions, and because, although it was possible to prepare from the leaf product a liquid of some activity, this as exceedingly feeble when compared with the actual powder itself, and did not give a satisfactory result. An air-dried sample of the young leaves of *I. arrecta* was employed throughout as a source of this product, and the yield was from 6·5 to 7 grams of a pale yellow powder from 10 grams of the material. The preparation of the enzyme powder from the old leaves of *I. sumatrana* was also experimented with, but the product was more resistant to the action of the alcohol, and the coloured substances could only be removed with considerable difficulty. Under the best conditions, the method is tedious, and with *I. arrecta* one and a-half litres of alcohol had to be employed as a rule for the purification of 10 grams of leaf. We are indebted to Prof. Beyerinck for a small quantity of his enzyme powder; this closely resembled our own specimens, and was exceedingly active. During the experiments recorded below, no special attempt was made to exclude bacterial action, for although in most instances this would be nullified by the temperature employed, the presence or absence of bacteria would little, if at all, affect the character of the results obtained. A difficulty not expected at first was due to the decay of the activity of the enzyme in the green leaf on long keeping, owing to the small amount of moisture there present, so that the preparations of the powder employed at the commencement of the investigation were considerably more active than those made at a later period. On the other hand, some compensation for this oversight has been afforded by the character of the results given by the less active powder.

In quantitative experiments on the hydrolysis of indican by the insoluble enzyme powder, special precautions are necessary on account of the oxidisable nature of the indoxyl produced and the difficulties of recovering any indigotin which thus separates. ter Meulen (*loc. cit.*), when investigating the extent of the hydrolysis by means of the condensation of indoxyl thus formed with isatin in feebly alkaline solution, did not attempt a separation of the enzyme and colouring matter, but, adopting certain precautions, calculated his results by the total increase in weight thus given. This method, although illustrating in his case the desired results, a point which has been previously discussed (this vol., p. 794) was not suitable in the present instance, as it was necessary to ascertain, not only the amount, but also the purity of the product obtained.

To avoid oxidation of the indoxyl during the fermentation, the preliminary experiments were conducted in a flask through which carbon dioxide was passing, but as minute traces of air could not be thus excluded, and this exercised an appreciable effect during the rather long periods required for complete fermentation, hydrogen was eventually employed and rendered free from air by passage through alkaline pyrogallol solution. To prevent a possible introduction of alkaline spray into the fermentation vessel, plugs of cotton wool were used to filter the purified gas.

In carrying out the operation the enzyme powder, ground into a thin cream with water, was introduced into a round Jena flask, the mixture made up to 500 c.c. by further addition of water, and then heated by a jacket of hot water to 45°, the temperature in all cases being noted by a thermometer placed in the flask itself. To remove air present in the water and adhering to the enzyme powder, the apparatus was evacuated, so that the mixture boiled vigorously, and a very slow current of hydrogen was subsequently passed for some time while the pump was still working, but finally much more rapidly. When air had been entirely removed, a stream of gas merely sufficient gently to agitate the enzyme powder was employed, and the solution of the indican (1 gram in 250 c.c.) was then introduced by means of a tap funnel. The reaction was at first most vigorous, and there was an almost immediate development of the deep green fluorescence so characteristic of indoxyl solutions. The inadvertent access of traces of air could always be detected by the formation of a faint coppery scum on the surface of the liquid, and whilst this was always present if carbon dioxide had been employed, it was scarcely ever to be noticed when this gas had been replaced by the purified hydrogen. As a rule, a faint trace of indigotin could always be detected in the enzyme powder at the conclusion of the experiment, and from this it could be removed by boiling acetic acid and estimated colorimetrically. The amount produced, however, during a well-conducted experiment was too trifling to merit consideration, as investigation showed that the quantity present did not average more than 0·2 per cent.

At the conclusion of the operation the flask and its contents were cooled to 17°, the passage of hydrogen being still continued, and after standing for a short time to allow the enzyme powder to settle, the clear liquid was decanted into a measuring cylinder and the residue into a second similar vessel. The indoxyl solution at this temperature was much more stable and less prone to oxidation than was at first suspected, and was thus not difficult to manipulate. The quantity of liquid present in both cylinders was noted, allowance being made for the enzyme powder, and 100 c.c.* of the clear solution were at once removed for a determination of the indoxyl it contained in the form of indirubin.

The process employed for this purpose consisted of introducing the 100 c.c. of liquid into a flask containing a boiling solution of 0·1 gram of isatin and 20 c.c. of hydrochloric acid in 200 c.c.* of water through which carbon dioxide or hydrogen was rapidly passing. After digesting for twenty minutes, the mixture was allowed to cool, and the beautiful, crystalline precipitate of indirubin was then collected on a tared filter, washed with dilute sodium hydroxide and acetic acid, as in the isatin method previously described (*J. Soc. Chem. Ind.*, 1907, **26**, 4, 1174), and the product weighed and analysed by means of titanium chloride under the conditions given by Bloxam (*ibid.*, 1906, **25**, 735). Simultaneously with the above operation, 400 c.c.* of the clear indoxyl solution, diluted to 850 c.c.* of water, were heated to 60° by means of a water jacket, and oxidised simultaneously by the passage of air through the liquid. The indigotin thus produced is, at least in part, in a state of pseudo-solution, and to obtain a complete precipitation of the colouring matter the mixture was digested at the boiling point for a short time with 25 c.c. of sulphuric acid. Filtration even then was of a tedious † character, and after washing with one per cent. sodium hydroxide solution, followed by 4 per cent. acetic acid, the product was weighed, and an aliquot portion sulphonated and analysed by the titanium method.

Finally, to ascertain if the indican had been completely hydrolysed by the enzyme, a third portion of the indoxyl solution was simultaneously oxidised by air, the indigotin completely precipitated by the addition of an excess of sodium sulphate to the mixture, and, after filtration, the clear liquid was treated with one or two drops of 2 per cent. ammonium persulphate solution and dilute sulphuric acid (4 per cent.) and gently warmed. If indican was present, a blue to a faintish green tint was produced, according to the quantity, and experiment has shown that it is possible to detect one part of pure indican in 20,000 of water by this test. It should be remarked, however, that with the coloured leaf extracts of *Indigoferae* the reaction is far less sensitive. A second and somewhat more rapid method, due to Beyerinck (*loc. cit.*), and also adopted by Bergtheil (*loc. cit.*), consists in oxidising the indoxyl solution in presence of a trace of ammonia, by which means the indigo separates in a more granular form, and after addition of a little hydrochloric acid in the cold, is thus more easy to filter. To be as far as possible assured of the absence of indican in the solutions of indoxyl which when tested in this manner had given a negative result, traces of indican were on certain occasions added to a fourth portion of the fermented liquid, but in all cases its presence could then be detected. The employment of titanium chloride for the analysis of the colouring matter was necessary, because the indigotin frequently contained some quantity of indirubin, and it has been shown by Rawson (*J. Soc. Dyers and Colourists*, 1899, **15**, 130) that in this case erroneous results are obtained when potassium permanganate is employed. In the analytical operation, the titration with the titanium chloride was usually carried out in the presence of purified hydrogen instead of carbon dioxide, and as the colouring matter given by crystalline indican is so much purer than that prepared from the plant extract under these conditions, the solution of the sulphonic acid was at once treated with the requisite amount of sodium tartrate and titrated without previous purification. Probably a slight defect in the analytical results is occasioned by the presence of a trace of enzyme powder which is carried down in the colouring matter thus isolated, and although Gaunt, Thomas, and Bloxam (*loc. cit.*) have shown that the indoxyl liquid can be filtered without apparent change by oxidation, and subsequently an elaborate apparatus for this purpose was devised, it was considered best to avoid any occasional risk of loss which might occur in this respect. It was ascertained that when traces of enzyme powder are heated with sulphuric acid, a pale brown liquid is formed, which on dilution is decolorised by the titanium chloride, but careful experiment has indicated that the colouring matter is not overestimated by this cause to the extent of more than one per cent. Again, an analysis of the indoxyl solution which had been filtered through cloth by the aid of the pump is given below, from which it is certain that little or no decrease of yield occurs if the filtration is carefully performed.

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* These proportions of liquid were employed in each case, and to avoid repetition they are not again referred to in the paper.

† On the average four days were necessary, in order to determine the results of each fermentation experiment.

The following table illustrates experiments carried out by the methods just described, the indoxyl solution being in this case oxidised without any previous addition of acid or alkali.

In every case the persulphate test indicated the absence of the glucoside at the conclusion of the experiment, and the residual enzyme powder was still found to evince considerable activity.

The results expressed in the table obviously show that whereas (*a*) the indoxyl solution decanted from the enzyme contains only 93 per cent. of the theoretical amount, (*b*) that the quantity of indigotin obtained by oxidising this liquid with air represents again a considerably lower value. In considering the first point (*a*), it is evident that even if the negative results of the persulphate test be

Time in hours.	Indican, grams.	Enzyme powder, grams.	Temp.	Indoxyl found, expressed as indigotin,* per cent.	Indigotin found, per cent.
2	1	2	50	93	—
2	1	2	50	93	82·0
2¼	1	2	50	93	—
2¼	1	2	50	94†	82·0†
4	1	2	50	93	83·0
5	1	2	30—32°	90	81·5
5	1	2	30—32	—	81·0
5	1	2	30—32	—	79·0

* In the estimation of indoxyl, according to the equation $C_8H_7ON + C_8H_5O_2N = H_2O + C_{16}H_{10}O_2N_2$, the indirubin produced represents, of course, double the amount of indigotin which the indoxyl can theoretically yield.

† Fermented liquid filtered before examination.

disregarded, any indican, presuming such was present, would, in addition to the indoxyl, be estimated as indirubin by the isatin method of analysis employed, so that the presence or absence of non-hydrolysed glucoside in the fermented liquid does not affect this part of the question.

On the other hand, it seemed possible that this deficiency in the amount of indoxyl observed might be due either to its partial occlusion by the enzyme powder or to its conversion into secondary products. To decide this question, experiments were carried out by the following method. A fermentation of 1 gram of indican with 2 grams of the enzyme was performed in the manner already detailed at 50° for two and a-quarter hours, and at the conclusion of the operation the mixture was treated in the presence of the hydrogen with 1 gram of isatin in 200 c.c. of water and 20 c.c. of hydrochloric acid. After a prolonged heating on the water-bath and subsequently cooling, the mixture of enzyme residue and indirubin thus produced was collected, washed, and dried, and, without removal from the filter paper, was extracted in a Soxhlet tube with boiling pyridine, which previous experiments (Trans., 1907, **91**, 279) had indicated to be one of the best solvents for indirubin. The extract was evaporated to a small bulk, treated with boiling water, and again distilled until all pyridine had disappeared. When cold, the beautiful crystalline precipitate of indirubin was collected on a tared filter, washed with 1 per cent. sodium hydroxide solution, weighed, and analysed by the titanium method (*loc. cit.*):

Found, indoxyl, represented as indigotin = 96·5 per cent.

In a second experiment, acetic acid was employed for the extraction instead of pyridine, but the operation in this case was of a tedious character:

Found, indoxyl, represented as indigotin = 96 per cent.

To complete the series an estimation of the indoxyl present after fermenting with the same proportions of glucoside and enzyme for five hours at 30° was carried out:

Found, indoxyl, represented as indigotin = 97 per cent.

It was noted that during this method of analysis no loss of indirubin took place, although it was observed that when treated with sodium hydroxide solution a trace of brown matter was removed from the crystals.

Evidently, therefore, from 3 to 4 per cent. of the indoxyl had been occluded by the 2 grams of enzyme powder under the above conditions, and thus the rather low percentage of indoxyl (93 per cent.) present in the fermented solution was in part accounted for.

As a final confirmation of this occluding property of the enzyme powder, the effect of larger amounts of this material was studied, employing the above method of analysis:

When 1 gram of indican and 4 grams of enzyme powder were allowed to react at 50° for four hours, the decanted liquid contained indoxyl, represented as indigotin = 89 per cent.

1 Gram of indican and 8 grams of enzyme powder at 50° for four hours gave in a similar manner indoxyl, represented as indigotin = 82·5 per cent.

No further proof of this point was therefore necessary.

These experiments therefore have accounted for 96 to 97 per cent. of the indican employed in the fermentations enumerated in the above table. From 3 to 4 per cent. of this colouring principle has thus undergone change into a product incapable, either by condensation with isatin or by oxidation, of giving either indirubin or indigotin in the usual manner. This loss may be represented to some extent by the brown impurity which contaminates the indirubin, and it was also noted that at the conclusion of the fermentation experiments the enzyme powder, originally of a pale yellow, then possessed a perceptible brown tint.

The most interesting point, however, arising from the experiments, and quite unanticipated, is the low yield of indigotin (88 per cent. approx.) obtained from the indoxyl actually present in the liquid by oxidation with air. As already pointed out, the persulphate method had indicated the absence of non-hydrolysed indican, but as the matter was so peculiar, a further test in this respect was employed. An indoxyl solution was oxidised with air as above, and the mixture was divided into two portions, the first of (*a*) which was proceeded with as usual and the indigo collected and analysed. To the second (*b*), at the boiling point in absence of air, 0·05 gram of isatin and 20 c.c. of hydrochloric acid were added, and the digestion continued for twenty minutes with the object of converting indican, if present, into indirubin. The results:

Found, indigotin *a* = 89·2, *b* = 85·8 per cent.

pointed clearly to the fact that an appreciable quantity of indican * did not exist in the fermented solutions, and that by addition of isatin the yield is less than usual. A second point suggested itself as possible, although most unlikely, and this was that indican, if present, might suffer alteration by the action of the air during the oxidation at 60°. This was, however, not the case, for equal quantities of a solution of the glucoside gave (*a*) before treatment with air, 0·1746 gram, and (*b*) after this operation 0·1720 gram indirubin.

Finally, experiments were made according to the method employed by ter Meulen (*loc. cit.*), in which the condensation of indoxyl with isatin is effected in feebly alkaline solution. These, carried out with the fermented liquid, were, unfortunately, not successful, as they yielded a smaller amount of indoxyl than that of the indigotin actually obtained from it, so that the details given in his paper are either not sufficiently clear or have been misunderstood by us.

In considering the deficient yield of the indigotin produced as above, after a minute examination of the process employed, attention was directed to the aqueous filtrate obtained when collecting this colouring matter. This acid liquid was invariably of a dull yellow colour, and although it was suspected at first that the tint had originated from the enzyme powder, blank experiments gave in this respect a negative result, and, moreover, when the original indoxyl solution had been filtered from the trace of insoluble enzyme, the yellow liquid was still produced. To account for this peculiarity, the presence of isatin suggested itself and an ethereal extract of this acid solution was examined. On evaporation, the residue consisted of a small quantity of a dull brownish-yellow resin, somewhat resembling the readily soluble, varnish-like compound which is formed to a small extent when indican is treated with boiling acid, and which is described in the preceding paper (this vol., p. 804). From this, however, the thiophen reaction could not be produced.

Again, some portion of the loss is probably accounted for by the fact that the indigo thus produced is contaminated with a trace of brown substance which is partly soluble in dilute alkali. The presence of this product was demonstrated by extracting some quantity of the crude colouring matter, prepared in a special experiment, with pyridine. To remove indirubin, which was also present, the liquid was treated with ether and then with an equal volume of water. As a result, the ethereal layer was red coloured, and the aqueous solution possessed a decided brown tint, due to the impurity in question, but it was evident that the latter was present in but small amount.

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* Theoretically (compare Croft Hill, Trans., 1898, **73**, 634), the presence of non-hydrolysed indican would be anticipated, but at the dilution employed the amount is evidently quite negligible.

Oxidation in Presence of Ammonia.

The oxidation of the fermented plant extract in the presence of ammonia was patented by Michea in 1876 (Rawson, *Report on the Cultivation and Manufacture of Indigo*, 2nd edition, 1907), is mentioned as beneficial by Georgewics (*Der Indigo*, 1892, 16), the point has been discussed by Rawson (*J. Soc. Dyers and Colourists*, 1899, **15**, 173). Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, **1**, 120) employed ammonia to facilitate the oxidation of the indoxyl, and mentions that the activity of the indigo enzyme is thus quickly destroyed, and a similar statement is given by P. van Romburgh (*ibid.*, 1899, **2**, 344). The more general employment of ammonia in India as an assistant in the factory oxidising process has resulted from the work of Rawson (*loc. cit.*), and its use in conjunction with the steam injector blower constitutes the most important improvement which he has recommended to the notice of the indigo planters. By the employment of this method, Rawson obtained increases in the yields of indigo varying from 24·1 to 63·8 per cent., and considers that the average increase in the colouring matter is about 34 per cent. as compared with that given by the ordinary oxidising process.

The following are the results which have been obtained by oxidising the fermented solution from pure indican with addition of varying quantities of ammonia.

Time, in hours.	Indican, grams.	Enzyme, grams.	Temp.	Indoxyl expressed as indigotin, per cent.	*N*/2-Ammonia, c.c.	Indigotin, per cent.
6	1	2	50°	92	18	86·0
6	1	2	50	—	18	86·5
5	1	2	50	92	18	86·0
5	1	2	50	—	18	86·0
5	1	2	50	93	36	85·0
5	1	2	50	92	72	82·5
5	1	2	50	92	180	80·5

If these figures are compared with those above given in the first table, it is evident that by the use of small quantities of ammonia during the oxidation process an increased amount of about 4 per cent. of indigotin is obtained. On the other hand, with more ammonia, the yield of indigotin is as low or even lower than that given when oxidation is carried out in the absence of this reagent. The effect, again, is not comparable with the striking results found by Rawson, and the behaviours of indoxyl produced from pure indican and indoxyl in presence of the indigo plant extract evidently vary considerably in this respect. The 4 per cent. larger yield recorded above is interesting in the light of the earlier experiments carried out under similar conditions of fermentation, but without ammonia in oxidising, as it affords a further proof of the conversion of indoxyl during oxidation into substances other than indigo.

The colouring matter thus obtained contains some quantity of indirubin, but this was only to be expected, as it is well known that the fermented plant extract when oxidised in the presence of ammonia and alkalis gives an indigo containing an appreciable amount of this red dyestuff. On the other hand, earlier experiments (Trans., 1907, **91**, 279) indicate that few, if any, samples of natural indigo are devoid of traces of this compound.

The Effect of Pure Oxygen.

The following experiments illustrate the effect of pure oxygen on the fermented liquid in the presence and absence of ammonia.

Time, in hours.	Indican, grams.	Enzyme, grams.	Temp.	Indoxyl as indigotin, per cent.	*N*/2-Ammonia, c.c.	Indigotin, per cent.
2¼	1	2	50°	93·0	none	78
2¼	1	2	50	93·5	,,	79
2¼	1	2	50	—	18	87

Thus the employment of pure oxygen with the neutral solutions of indoxyl gives 3 to 4 per cent. less colouring matter than is obtained when air alone is employed, whereas in presence of ammonia the yield is but little affected. These results are most probably accounted for on the assumption that some isatin is produced during the oxidation which in the first case is lost, but in the latter, owing to the presence of ammonia, condenses to form indirubin. In support of this suggestion the colouring matter from this ammonia experiment on analysis was estimated to contain approximately 9 per cent. of indigo-red.

Oxidation in Presence of Lime-water.

The employment of lime during indigo manufacture, both in the fermentation and oxidation vats, in order to effect the more ready precipitation of the colouring matter has long been known, and in Crookes' *Handbook of Dyeing and Calico Printing* (1874, 451) is mentioned in connexion with Chinese indigo, and also in regard to the Manilla variety. More recently it has formed the essential feature of the Coventry process in India, and is added to the fermented liquid before oxidising in a special vat. A considerable quantity of mineral matter derived from the plant is thus precipitated, and the clear liquid is readily susceptible to oxidation. Rawson (*loc. cit.*) has stated that by this process in the laboratory the average increase in the yield of colouring matter is 18·2 per cent. Experiments on this point, employing indican, gave results closely resembling those obtained with ammonia as regards the percentage of indigotin to the indoxyl produced. The low yield of indoxyl recorded in experiment (*A*) is due to a cause which will be discussed later.

	Time, in hours.	Indican, grams.	Enzyme, grams.	Lime-water, c.c.	$N/2$-Ammonia, c.c.	Indoxyl as indigotin, per cent.	Indigotin, per cent.
A	7½	1	2	20	—	87·3	81·5
	7½	1	2	20	18	—	81·3
B	2¼	1	2	220	—	92·0	77·0

For the purpose of comparison the oxidation of a portion of the same fermented liquid in presence of ammonia was carried out, and the results are in this case best understood by comparing the percentage of indigotin found to the indoxyl actually present before oxidation.

As was previously shown to be the case with ammonia, an excess of lime-water is thus detrimental. The statement of Rawson (*loc. cit.*), that the reagent is best added to the fermented solution until a faint alkalinity is observed, is borne out by these results. As is well known, the "Coventry" indigo contains much indirubin, and this was the case with regard to the samples prepared under the above conditions.

Effect of Potassium Acetate during Oxidation.

It was considered possible that the presence of this salt might facilitate oxidation of the indoxyl, but experiment showed that it exerted, however, a remarkable contrary effect.

Time, in hours.	Indican, grams.	Enzyme, grams.	Temp.	Potassium acetate, grams.	Indoxyl as indigotin, per cent.	Indigotin, per cent.
7½	1	2	50°	0·88	87·5	69·5
2½	1	2	50	5·0	—	71·0
2½	1	2	50	5·0	—	71·5

This low yield of indigotin was accounted for by the appearance of the filtrate obtained from it, which possessed a rich dichromate colour in each experiment. This point will be further investigated as soon as opportunity arises.

The Employment of Sodium Nitrate during Fermentation.

The addition of Chili saltpetre to the fermentation vat has been a custom among Indian planters for some time past, and Rawson (*loc. cit.*) states that although no increase of the colouring matter is thus produced in the oxidation vat, the precipitate settles better, and is more easily collected. An experiment in which 1 gram of indican was fermented with 2 grams of enzyme at 50° for two and a-quarter hours in presence of 5 grams of sodium nitrate under the usual conditions, gave:

Indoxyl, as indigotin = 93 per cent. Indigotin = 81 per cent.

results closely similar to those given above, which were obtained without the employment of this chemical.

Fermentation in Presence of Acid.

According to Beyerinck (*loc. cit.*), great attention should be paid to the degree of acidity of indican solutions which are undergoing fermentation, and he states that the most favourable result is obtained when 0·5 c.c. of normal acid is added to 1000 c.c. of the liquid. On the other hand, with 2 c.c. of the acid the enzyme action is notably slackened. Bergtheil (*loc. cit.*) considers that the action proceeds quite normally in presence of 0·01 or 0·005 per cent. of hydrochloric acid in the case of the plant extract.

The following are the results of experiments in which sulphuric acid was added to the fermentation mixture. The indoxyl solution was subsequently rendered alkaline with ammonia to the same extent (18 c.c. of *N*/2-ammonia) as before and then oxidised.

Time, in hours.	Indican, grams.	Enzyme, grams.	Temp.	*N*/10-Sulphuric acid, c.c.	Indoxyl expressed as indigotin, per cent.	Indigotin, per cent.
5½	1	2	50°	3·7	94·5	89
5½	1	2	50	3·7	95·0	90

It was thus evident that by the employment of this small amount of acid under the conditions given above, an increase of colouring matter is obtained, and this is probably due to the fact that the acid tends to inhibit the conversion of indoxyl into secondary products, and to some extent prevents its occlusion by the enzyme powder. There is no doubt that acid solutions of indoxyl are less prone to oxidation, and experiment has indicated that the cold, moderately acid liquids are of a comparatively stable nature, as, indeed, the work of Beyerinck (*loc. cit.*) also shows.

These points received confirmation in the following manner. In an experiment carried out exactly as above, and when the fermentation had proceeded for five hours, a further quantity of 10 c.c. of the acid was added to the mixture and the process continued for fifteen minutes longer. The indoxyl was determined as indirubin, and the yield was 99·5 per cent. of the theoretical quantity.

The indoxyl, therefore, in the form of its sulphate is not occluded by the enzyme powder, and in the presence of the 3·7 c.c. of the acid under the above conditions was not appreciably destroyed by secondary change.

Oxidation in Presence of Acid.

Having previously obtained a favourable yield of indigotin (this vol., p. 802) by the simultaneous hydrolysis of indican with hydrochloric acid and oxidation with air (93·5 per cent.), experiments on the aerial oxidation of the acidified fermented liquid were carried out. The results are expressed as the amount of indigotin obtained in proportion to the indoxyl actually present in the solution, and the quantities of hydrochloric acid (33 per cent.) employed were respectively (*a*) 3·0 per cent. and (*b*) 0·28 per cent.:

Found, indigotin (*a*) = 91, (*b*) = 91·7 per cent.

Within these limits the proportion of acid present in the solution during oxidation somewhat improves the result, and the yield of colouring matter is very similar to that produced (approx. 92·5 per cent.) when a small amount of ammonia is thus employed. In the presence of acid, however, a prolonged oxidation is necessary, and it is to be remarked that the product contains some quantity of indirubin together with a brown impurity.

Effect of Temperature during Oxidation.

It was evident that when a solution of indoxyl is oxidised by air at 60° an amount of colouring matter considerably lower than that required by theory is produced, and as it was possible that this effect might be the result of the temperature employed, an oxidation was carried out at 30°. Two grams of indican and 4 grams of the enzyme were allowed to react in the usual manner for seven hours at 50°. A portion of the indoxyl solution (*a*) was oxidised at 30° without addition of ammonia for three and a-half hours, and (*b*) for purposes of comparison a second quantity of the same liquid was treated with ammonia and oxidised as usual at 60°:

Found, indoxyl, represented as indigotin = 90. Found, indigotin (*a*) = 80, (*b*) = 83·5 per cent.

There was accordingly scarcely any perceptible difference between this result of an oxidation of the indoxyl solution at 30° and those previously obtained by the employment of the higher temperature. If anything, the proportion of indigotin to indoxyl produced at the lower temperature is less than usual, but when compared with the colouring matter produced by the alkaline oxidation at 60° the proportions are, on the other hand, very similar to those given in former experiments.

Prolonged Fermentation.

The tendency of the fermented plant extract, if kept before oxidation, to suffer a loss of indoxyl is well known. Rawson (*loc. cit.*), for instance, states, "Under such conditions there is always a loss of colouring matter," and "a loss of 7 per cent. took place in three hours, and as much as 16 per cent. on standing six hours." "When using the hot water process . . . the liquid should almost always be immediately oxidised, otherwise changes rapidly take place, resulting in the loss of much colouring matter."

As previously suggested, the behaviour of a solution containing almost pure indoxyl and a fermented plant extract may exhibit considerable differences on account of the numerous impurities present in the latter, so that it was interesting to study this point with the pure glucoside.

One gram of indican and 2 grams of enzyme were digested together under the usual conditions for ten hours, and the indoxyl in the clear liquid determined as indirubin:

Found, 86·5 per cent.

The average result, as above stated, is 93 per cent. in a rapid fermentation, so that the loss of indoxyl thus occasioned is approximately 6·5 per cent.

To ascertain the total quantity of indoxyl present in the mixture, some of which as previously shown is occluded by the enzyme powder, a second similar experiment was carried out, and the whole product, including the powder, then treated with isatin and acid as has been described earlier in the paper. The insoluble matter was collected, the indirubin isolated by means of pyridine, and analysed:

Found, 90 per cent.

In a ten hours' fermentation, therefore, the actual loss of indoxyl was 10 per cent.

To obtain further evidence on this point, a fermentation was allowed to proceed for thirty hours at 50°, and in this case, not only the indoxyl, but the yield of indigotin produced from it was also ascertained by oxidation in the presence of ammonia:

Found, indoxyl as indigotin = 76·5. Indigotin = 71 per cent.

At the conclusion of this operation the enzyme powder possessed a dark brown colour, and the acid filtrate from the indigo had a deep reddish-brown tint, and resembled in appearance a strong aqueous solution of isatin. The colouring matter also yielded to dilute alkali a larger quantity of a brown impurity than usual.

Finally, to determine if indoxyl solutions were stable at the ordinary temperature (15° approx.), a fermentation experiment was carried out at 50° with 1 gram of indican and 2 grams of the enzyme. After hydrolysis was complete, the mixture was then kept at 15° in an atmosphere of hydrogen for twenty-one hours. In this case the liquid was oxidised by air in the absence of ammonia:

Found, indigotin = 79 per cent.

As indicated by earlier experiments, the yield of colouring matter in ordinary circumstances would average 82 per cent. Indoxyl solution at 15° in absence of air is thus fairly stable, the loss on keeping for twenty-one hours being in this case but 3 per cent. approximately.

In connexion with this portion of this subject, the decay of the activity of the enzyme in the air-dried leaf previously alluded to can be discussed. This is also accompanied by a slow disappearance of the indican present, which has been referred to in the preceding paper (this vol., p. 805).

The earliest preparations of enzyme powder were made during October, 1907, from leaf received from India in May, and these were the most active, as 2 grams of the material were capable of hydrolysing one gram of indican in at least two hours. A considerable quantity of the powder was prepared at, or about, that period, but later samples made from the same leaf in May, 1908, showed that a deterioration of the activity had occurred, and that for hydrolysis under the same conditions about five and a-half hours were necessary. Finally, enzyme powder made in October, 1908, again from the same leaf, exhibited a further diminution of activity, for, employing this, seven and a-half hours were required before the hydrolysis was concluded. On the other hand, the enzyme powder preparations after drying did not themselves, as was to be expected, exhibit any loss of hydrolytic power on keeping.

Certain of the experiments illustrating these points are interspersed among the results already given, and it will be only necessary to allude to those obtained with the least active enzyme preparations, as it is thus shown that during the longer period which was necessary for the complete hydrolysis a loss of indoxyl has taken place. For the purposes of comparison, an experiment (*A*) with a more active powder is appended.

Time, in hours.	Indican, grams.	Enzyme, grams.	Temp.	Indoxyl expressed as indigotin, per cent.	*N*/2-Ammonia, c.c.	Indigotin found, per cent.
2¼	1	2	50°	92·0	18	86·0
7½	1	2	50	87·5	—	—
(*A*) 7½	1	2	50	88·0	none	78·5
7½	1	2	50	87·3	18	81·3
7½	1	2	50	87·5	—	—

It is interesting to note that although it is evident that these pure solutions of indoxyl gradually decay under the above circumstances, the losses produced are not so severe as those found by Rawson (*loc. cit.*) to occur with the much more impure fermented indigo plant extract. On the other hand, Rawson's figures represent the disappearance of the colouring principle when the solution has been kept after fementation, and do not refer to those taking place during the fermentation itself. There can be no reason to suppose that the disappearance of indoxyl only commences when the final trace of indican in the liquid has undergone hydrolysis, or that any prevention of this indoxyl decay is afforded to its solution by the presence of the still active enzyme in the accompanying leaf debris. It is evident that the tendency of indoxyl to behave in this manner is one of its inherent properties, and that the slow change or condensation which takes place, resulting in the formation of a product incapable of giving indigotin by oxidation, will commence to occur at the moment of its liberation from the indican. This point is not suggested to be novel, but, on the other hand, the statements of Bergthiel (*loc. cit.*, p. 879), "a decrease in the amount of indigotin obtainable . . . . takes place if the fermented solution is allowed to stand after fermentation is complete," * and also that of Rawson (*loc. cit.*, p. 58), "The liquid after steeping deteriorates on standing," do not leave one to infer that this change will also occur during fermentation. As regards the much greater disappearances of indoxyl observed by these authors in connexion with the plant extracts, and those recorded as occurring with the fermented solutions derived from pure indican, it suggested itself at first that these might probably owe this increased loss to a condensation of indoxyl with ketonic or aldehydic substances derived from the plant itself, but there is evidence that such a reaction does not take place, at least, to any great extent, and that the effect in question is due to other causes.

The Solubility of the Enzyme.

Bergtheil (*loc. cit.*) considers that the insolubility of the enzyme as contained in the leaf of *I. sumatrana* arises from the presence of tannin (compare Brown and Morris, Trans., 1893, **63**, 604, and Mann, *J. Asiatic Soc. Bengal*, 1901, **70**, 154) and states that by the aid of hide powder he was enabled to obtain "a very active solution of the enzyme." The matter has been discussed by Gaunt, Thomas, and Bloxam (*loc. cit.*), who have pointed out that Bergtheil's product is not a true solution, as the enzyme present is entirely removed by a Berkfeld filter. Bergtheil (*J. Soc. Chem. Ind.*, 1907, **26**, 70) admits this to be the case, but states that his liquid may be termed a "colloid solution." On the other hand, Bergtheil, in his original communication (*loc. cit.*), does not record any examination of the leaves of *I. sumatrana* or *I. arrecta* for tannin, and as the results of tannin analyses of these materials given in a paper by Perkin and Bloxam (Trans., 1907, **91**, 77) did not give a certain indication of this substance for reasons there stated, the presence or absence of tannin in these leaves had yet to be decided.

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* This point is illustrated by Bergtheil (*loc. cit.*), who obtained, after a 20 hours' fermentation of a sample of plant extract, the reaction being then complete, 0·096 gram of indigotin. On allowing a portion of the same solution still containing the enzyme to remain for 16 hours longer, the yield was 0·0547 gram of indigotin, representing a loss of nearly 40 per cent.

The experiments carried out in this investigation have had as their starting point the purified enzyme powder as prepared by the Dutch chemists (*loc. cit.*), and any tannin matter, if originally present, would be eliminated during the repeated extraction of the material with alcohol. When shaken with water, this enzyme powder could be freed only with difficulty from adherent air particles, but this was overcome by evacuating the flask which contained the mixture. By operating in this way at the ordinary temperature and at 50°, but without adopting precautions to exclude bacteria, and subsequently filtering through paper, active liquids were produced. These products had not the characteristics of true solutions, as their activity could be diminished considerably by refiltrations through ordinary filter paper, and, again, when the solutions were examined by strong sunlight the presence of very minute particles in suspension could be observed.

For the purpose of a fermentation experiment, a quantity of the enzyme powder was extracted with 600 c.c. of water at 50° with evacuation of air, and the liquid was then decanted and filtered twice through ordinary filter paper. The whole of the extract was employed for the hydrolysis of one gram of indican at 50°, and, after a digestion for seven and a-half hours, the following result was obtained:

Found, indoxyl expressed as indigotin = 88 per cent. Found, indigotin = 74 per cent.

here was every evidence that the reaction took place much more slowly than had been the case when the enzyme powder had been employed, and there could be no doubt that the liquid was of an extremely feeble character by comparison. The result indicates that even after this lengthy period of incubation, the hydrolysis of the glucoside was still incomplete, and again it has been shown that a satisfactory yield of colouring matter cannot be obtained owing to the disappearance of indoxyl unless the reaction takes place rapidly. It is quite possible that by treating very large quantities of the powder with water in the above manner, more active liquids might be produced, but the difficulties involved in the preparation of any great amount of this material did not render further investigation of this point worth while. Our results, therefore, are in harmony with those of the Dutch chemists, in that it is not possible to obtain a true solution of the indigo enzyme.

A point of interest arising from the above experiment is the fact that on washing with dilute alkali, the usual small quantity of brown matter was removed from the indigo thus obtained, from which it appears that this can only be of an indoxylic character and is not derived from the enzyme powder.

The Oxidation of Solutions of Synthetic Indoxyl.

We are much indebted to the firm of C. A. F. Kahlbaum, in Berlin, for an attempt, at our request, to prepare a sample of indoxyl for the purposes of this investigation; unfortunately, however, owing to the unstable nature of the substance, they found themselves after experiment unable to comply with our wish. On the other hand, they were good enough to present us with 5 grams of crude indoxylic acid, with which the following experiments were carried out.

It is well known that on boiling an aqueous solution of indoxylic acid decomposition ensues with formation of indoxyl, and this process was now carried out in an atmosphere of hydrogen. After cooling, the fluorescent liquid was filtered, and this could be conducted at the ordinary temperature without apparent loss. The first experiments on the oxidation of this solution were unsatisfactory, because it was found that, in addition to indoxyl, unchanged indoxylic acid was present in small amount, and this was indicated by the extremely dark brown liquid which was produced when the oxidised liquid was boiled with dilute acid and filtered.

It was ascertained, however, that if the solution given by indoxylic acid was treated at 60° with ammonia at the concentration indicated below, it was entirely converted into indoxyl, for when the colouring matter produced by oxidation with air was collected, the clear filtrate gave no coloration with persulphate and acid.

In order to study quantitatively the yield of colouring matter given by the indoxyl when oxidised by air in presence of ammonia, 1 gram of the indoxylic acid was treated with 500 c.c. of water, and the mixture heated in absence of air to 90° for half an hour. When cold, the product was filtered and the liquid diluted to 600 c.c., and 100 c.c. then withdrawn and analysed by the isatin method. As a result, the amount of pure indirubin obtained from the latter was 0·0735 gram, which represented an indigotin value of 0·03675 gram for the 100 c.c. of liquid.

Four hundred c.c. of the same solution, diluted to 850 c.c. and treated with 18 c.c. of $N/2$-ammonia, on oxidation with air at 60° gave indigo, which on analysis was found to represent 0·1363 gram of pure colouring matter. The indigotin value of this quantity of liquid being 0·1470 gram, the yield thus obtained was 92·8 per cent.

A second experiment, employing 0·6 gram of the indoxylic acid, was carried out in a similar manner, with the exception that the decomposition was effected at the boiling point and not at 90°. The indigotin value of the solution was in this case 0·0990 gram, whereas the pure colouring matter formed by the oxidation was 0·0905 gram. Yield 91·5 per cent. The average of these two results is 92·15 per cent., and this figure is practically identical with those given by the ammoniacal oxidation of indoxyl produced by the hydrolysis of indican by means of the enzyme, which have been enumerated above.

The loss occasioned by the oxidation of the synthetical indoxyl was to be accounted for by the coloured appearance of the indigo filtrate, and by the fact that the colouring matter thus obtained contained a small amount of a brown compound. There can be no doubt, therefore, that under these conditions it is not possible to obtain a theoretical yield of indigotin from indoxyl.

Experiments on the oxidation of indoxyl derived from indoxylic acid by means of air in the absence of ammonia did not give a satisfactory result, on account of the difficulty of completely decomposing this acid by digesting its solution at the boiling point. After two unsuccessful trials, which gave very imperfect yields of indigo,* it seemed possible that by the addition of ammonia to the mixture after the usual period of oxidation the unattacked indoxylic acid would be thus decomposed and a better result might be obtained. Remarkably enough, no improvement was found to be effected in this manner, and it thus seems certain that when a solution of indoxylic acid is oxidised with air at 60°, it is converted, at least in part, into a substance other than indigotin, and in this respect resembles indoxyl itself. It was observed, for instance, that when the ammonia was added in the manner above indicated a rich brown colour was produced in the supernatant liquid, and this it appeared could only be due to some compound derived from the indoxylic acid. Owing to lack of material this interesting point has not up to the present been further examined.

Preliminary experiments have been carried out on the fermentation of the aqueous extract of *I. sumatrana* by means of the enzyme powder, with the result that up to the present the yield of colouring matter has been much lower than that given by pure indican itself. A definite statement on this point is, however, reserved until a more elaborate study of the matter is possible, because, not only are the necessary operations more difficult to carry out than those with pure indican, but also because a new supply of freshly-gathered leaf will be essential for this purpose.

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* The yields of indigotin thus obtained were respectively 47 and 48 per cent.

In conclusion, it may be said that details of the analysis, such as the weights of the colouring matter obtained and the purity of the products, have been omitted from this paper on account of their minor interest. The analyses in every case have been performed in duplicate, and the methods rigidly standardised by means of the chemically-pure dyestuffs, and although it has been pointed out that the results are probably a little too high, it will be evident that as the same method has been employed under identical conditions for the analysis of both indigotin and indirubin, the relationship of the figures to one another will be very closely correct. Certain points of considerable importance, such as the effect of organic acids on the fermentation process, have not as yet been studied, but these will be undertaken as soon as opportunity occurs.

Summary.

The results of this investigation show that when pure indican is hydrolysed by its specific enzyme, indimulsin, and the indoxyl solution thus obtained is oxidised with air, considerably less than a quantitative yield of indigotin admixed, or otherwise, with indirubin is thus produced.

This is partly explained by the fact that the solution of indoxyl, even in an atmosphere of hydrogen, is not stable, but is slowly converted into a product which is incapable of yielding indigotin on oxidation. This property, which may be referred to as the "decay" of indoxyl, can even be observed if the enzyme hydrolysis has been rapid, but its effect is much more evident when, owing to the feebler activity of the indimulsin, a longer period has been required to complete the reaction.

If, however, a small quantity of sulphuric acid is added to the mixture at the commencement of the fermentation, this "decay" of indoxyl is avoided to a considerable extent, and the acid, moreover, has a further beneficial effect in that it prevents the occlusion of indoxyl by the enzyme powder, which otherwise always occurs. Beyerinck (*loc. cit.*), it is worthy of note, has stated, in reference to the purified plant extract, that in the presence of a minute quantity of acid the enzyme hydrolysis proceeds more rapidly, and this is considered by him to be a point of much importance. Somewhat remarkable is the secondary reaction which occurs simultaneously with the production of the colouring matter when the indoxyl solution is oxidised by air, and this, as the experiments have illustrated, is to a considerable extent responsible for the deficient yield above referred to.

On the other hand, Baumann and Tiemann state (*Ber.*, 1880, **13**,414) that indoxyl is quantitatively converted into indigotin by means of oxidising agents. Unfortunately, the experimental details are not given in their paper, but as at that time no trustworthy methods had been devised for ascertaining the purity either of indoxyl or of the indigotin derived from it, their opinion on this point cannot be considered correct.

In regard to the chemical nature of the change which takes place during the "decay" of indoxyl, or of the secondary reaction which occurs during the oxidation of its solution by means of air, there is as yet no certain evidence. The isolation, however, of substances which in character resemble indoxyl-brown or indigo-brown, although but in small amount, indicates the effect, at least in part, of a condensation similar in character to that which is involved in the production of the former product. It is interesting to note that whereas this secondary change is greatly facilitated by the presence of potassium acetate during the oxidation, it is retarded by the addition of a small quantity of ammonia or lime-water, and the best yields of colouring matter are consequently given when the indoxyl solution previous to oxidation is treated with the latter reagents.

It seems possible that this peculiar behaviour of indoxyl may be due to the existence of one of its tautomeric forms, and that, for instance, pseudo-indoxyl is responsible for the by-products under discussion, and that these are formed while indigotin is being simultaneously produced from indoxyl itself. Another feature of the oxidation is the formation in certain circumstances of some quantity of indirubin, and it is well known that this occurs during the manufacture of natural indigo when the fermented plant extract is oxidised under slightly alkaline conditions. A similar result has been obtained in these laboratory experiments with the purer indoxyl solutions, and, peculiarly enough, it has also been found during the preceding investigation (*loc. cit.*) that oxidation in the presence of acid has a similar, although perhaps more strongly marked, effect.

For the formation of indirubin, isatin is necessary, and as it can hardly be presumed that the latter substance is derived from the indigotin at first produced by further oxidation with the air, it originates without doubt directly from indoxyl itself. It has, in fact, been shown by the Badische Anilin- und Soda-Fabrik (D.R.-P. 107719) that by means of suitable oxidising agents, not, however, including air, indoxyl can be converted into isatin without a previous formation of indigotin, and a peculiar instance of this effect has recently come to light and is described in the following communication (this vol., p. 847).

As a result, therefore, of the employment of acid during the enzyme hydrolysis of indican, and oxidation of the resulting indoxyl solution under the feebly alkaline conditions given above, the best yields of colouring matter have been obtained. On the other hand, it has not been found possible either with synthetical indoxyl or indoxyl derived from indican to obtain a quantitative yield of pure indigotin or of an admixture of this colouring matter with indirubin. Preliminary experiments on the production of indigo from an aqueous extract of the leaves of *I. sumatrana*, and employing enzyme hydrolysis, have, as yet, given results of a far from quantitative character, but the matter is still under investigation. There is, however, evidence from the results of Rawson and also of Bergtheil (*loc. cit.*) that in the case of the fermented plant extract a more rapid decay of indoxyl takes place than is observed under laboratory conditions with the purer solutions of this colouring principle.

It is a matter of general agreement that the imperfect yield of natural indigo obtained on the manufacturing scale is due to (*a*) a retention by the plant residue after fermentation of some of the colouring principle, and (*b*) from the incomplete settlement of the finely divided colouring matter produced by the oxidation. On the other hand, (*c*) the decay of indoxyl during both fermentation and oxidation cannot but have an important bearing on this point.

(*a*) The quantity of colouring principle thus retained is estimated by Rawson (*loc. cit.*) to be about 5 per cent., and his experiments indicated that this could not be satisfactorily recovered by a second steeping of the plant residue.

Although the proportion of enzyme powder to indican present in the fresh leaf of *I. sumatrana* will be at least nine times greater than that generally employed in this paper, the difference between the physical nature of the leaf after fermentation and the purified laboratory material does not allow of any direct inference as to the amount of indoxyl occluded by the former during the manufacturing process, but it seems possible, as a result of this work, that more of the indoxyl may be thus retained than is believed to be the case. On the other hand, a second steeping or washing of the leaf residue with water containing a trace of sulphuric acid is suggested as worthy of experiment, for it has been shown that this occlusion of indoxyl does not occur in presence of the acid, and, moreover, that the acid solutions of this colouring principle possess considerable stability.

(*c*) More interesting would be the study of the effect of the addition of acid to the fermentation vat in small proportion at the commencement of the operation for the reasons discussed earlier, and it is to be noted that a further addition at the conclusion of the hydrolysis would possibly be advantageous. As the plant extract, however, contains in solution the calcium and other salts of organic acids, by the use of sulphuric acid the acidity of the liquid will be due to the liberation of the latter, and it is therefore likely that the direct employment of oxalic acid would be of service.

(*b*) It has been shown (*loc. cit.*) that the most satisfactory laboratory results on the preparation of indigotin from the plant extract, and also from pure indican, are given when the solution is hydrolysed by hydrochloric acid with simultaneous oxidation by air. If such a process could be economically employed on the manufacturing scale, the somewhat serious losses, which are acknowledged to occur by an incomplete deposition of the precipitated colouring matter, should be avoided, although, on the other hand, the cost of hot water extraction of the plant is considered by Rawson (*loc. cit.*) to be prohibitive.

We are indebted to the India Office for a grant which has been, in part, employed to cover the expenses of this investigation, and to Sir Thomas Holderness, K.C.S.I., for his kind interest and trouble in the matter.

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LEEDS.

XCIII.—*Indoxylic Acid.*

By ARTHUR GEORGE PERKIN.

DURING experiments on the aerial oxidation of indoxyl which had been prepared by the enzyme hydrolysis of indican (preceding paper) it appeared to be of interest to confirm the results obtained by an examination of the oxidation of synthetical indoxyl, and it seemed likely that commercial indoxylic acid would be an excellent source of this substance, which is otherwise difficult to isolate in a pure condition. Commercial indoxylic acid was for a short time placed on the market under the name of "indophor," because, owing to the readiness with which it is converted into indoxyl, and the latter by oxidation into indigotin, it was found suitable for calico-printing purposes. As the result of a search in this department of the University, two specimens bearing the correct label were discovered, but these had evidently undergone some alteration, for whereas indoxylic acid is colourless, both bottles contained a dull reddish-violet powder. Experiment showed that whereas in one of these (*A*) indoxylic acid was entirely absent, in the second (*B*) a trace still existed, but this did not yield sufficient indoxyl for a satisfactory oxidation experiment. As this decomposition of indoxylic acid appeared to be, not only remarkable, but also interesting, owing to the fact that its behaviour seemed likely to throw light on some points observed during the oxidation of indoxyl derived from indican, the substances produced were subjected to investigation.

The sample *A*, which weighed approximately 6 grams, and in which indoxylic acid was entirely absent, was the most carefully examined, and as experiment indicated the presence of a substance or substances soluble in alkali, it was in the first place completely exhausted with boiling 1 per cent. sodium hydroxide solution. The deep brown solution was acidified, the resulting brown precipitate was collected, and the filtrate (*C*) reserved for further examination. For the purpose of purification the brown precipitate was dissolved in boiling pyridine, the solution filtered from a trace of insoluble matter, and the filtrate treated at the boiling point with sufficient alcohol to precipitate an almost black substance, which was present in small quantity. This was removed by filtration, and to the clear liquid an excess of ether was added; this caused the separation of a voluminous, dull brown precipitate, which was collected and washed repeatedly with pure ether until the washings were colourless. The filtrate contained a small quantity of indirubin. The product, which resembled indigo-brown, possessed, like this substance, the property of obstinately retaining moisture, and was therefore dried at 160°:

Found, C = 67·35; H = 3·68; N = 9·94 per cent.

These analytical figures somewhat resemble those previously found for the main constituent of indigo-brown (Trans., 1907, **91**, 279), to which the provisional formula $C_{16}H_{12}O_3N_2$ (C = 68·57; H = 4·28; N = 10·00 per cent.) was assigned, and this result, together with other properties, suggest as probable that it may consist of a slightly impure form of the natural indigo-brown compound. The amount available after analysis was too small to admit of a further treatment by the fractional precipitation methods, but it was ascertained that although the main bulk of the product was homogeneous, and could only be dissolved by means of pyridine, traces of substances soluble respectively in alcohol and acetic acid were also present. It is interesting to note that crude indigo-brown also contains small quantities of more readily soluble substances, the percentage of carbon in which is somewhat lower than that of the main constituent, for which the best solvent is also pyridine. The product from indoxylic acid dissolved in alkaline solutions with a deep brown coloration, and was converted by means of nitric acid into a dull orange-yellow, amorphous product. It possessed no definite melting point, but when destructively distilled it swelled up and evolved vapour, which condensed to form a small quantity of a brown, oily matter.

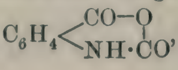
That portion of the original specimen (*A*) which was insoluble in alkali was dried and repeatedly extracted with small quantities of boiling pyridine, when the main portion of the substance passed into solution, and it was observed that, whereas the first extracts possessed a deep red colour, the latter were slightly bluer, and these were accordingly kept apart. On evaporating the pyridine solutions at first obtained to a small bulk, crystals separated on cooling, and these were further purified by means of the same solvent:

Found, C = 73·19; H = 3·95; N = 10·72.
$C_{16}H_{10}O_2N_2$ requires C = 73·28; H = 3·81; N = 10·69 per cent.

This analysis, and the examination of its properties, clearly proved that this, the main constituent of the original powder (*A*), was indirubin. The small amount of substance which remained after the removal of the indirubin was crystallised from nitrobenzene, and had, as was expected, all the properties of indigotin:

Found, N = 10·75. $C_{16}H_{10}O_2N_2$ requires N = 10·69 per cent.

Attention was now directed to the aqueous filtrate (*C*) (p. 848) obtained during the isolation of the brown compound, and this was repeatedly extracted with ether and the ethereal solution evaporated. The semi-crystalline residue was digested with a small quantity of boiling benzene, the hot liquid decanted, and a brown, gelatinous product, which separated on cooling, was removed and the filtrate allowed to evaporate spontaneously. Orange-coloured needles were slowly deposited, but in too meagre an amount for efficient purification; on the other hand, as they readily gave with sulphuric acid and commercial benzene the thiophen reaction, there could be no doubt that they consisted mainly of isatin.

The residue insoluble in benzene was dissolved in a small quantity of hot alcohol, and, on cooling, crystals separated; these, after repeated purification by means of the same solvent and a final crystallisation from water, consisted of almost colourless needles, and possessed the properties of an acid. When slowly heated, this acid melted with effervescence at about 215°, but a melting point as high as 223° could be obtained by heating more rapidly. Most probably this compound is phenylglycine-*o*-carboxylic acid, and this receives support from the fact that in a patent of 1894 the Badische Anilin- & Soda-Fabrik describes the preparation of indoxylic acid by heating the sodium salt of this substance with alkali, for it is quite likely that in such a process a trace of the original acid would escape conversion. In general physical properties it also resembled isatoic acid,  $C_6H_4{<}\begin{matrix}CO-O\\ NH\cdot CO\end{matrix}$, but this, however, is said to melt at 230°.

An approximate analysis of this sample of indophor (*A*) gave the following amounts of the main constituents mentioned above.

Matter soluble in alkali	32·94 per cent.
Indirubin..............................	42·37 ,,
Indigotin..............................	17·30 ,,
Moisture	2·15 ,,
Ash	1·05 ,,

Of the matter soluble in alkali, approximately one-half (15·44 per cent.) consisted of the crude brown product above discussed, and the remainder is accounted for by the presence of other brown substances of a more soluble character, together with the phenylglycinecarboxylic acid.

The analysis of the indirubin and indigotin was carried out by a comparison of the strength and shade of the sulphonated mixture with similar solutions obtained from the chemically pure colouring matters in a Duboscq tintometer. The purity of this material was thus shown to be 89 per cent., and it was contaminated with a fibrous substance insoluble in nitrobenzene, which no doubt accounts for the deficit in the above analysis.

An examination of the sample *B*, in which a trace of indoxylic acid was found to be present, indicated that it contained the same brown substance as *A*, but to a less extent, namely, 6·41 per cent. Curiously enough the proportion of indirubin to indigotin in this specimen was found to be as 70 to 30, and this result is almost identical with that given by the investigation of the sample *A*, in which the proportion of these colouring matters was as 71 to 29. Determinations of ash and moisture gave respectively 1·38 and 4·79 per cent.

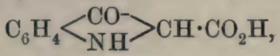
In considering the reactions which have been involved in this conversion of indoxylic acid into indigotin and indirubin, the presence of the former does not require special comment, for it is well known that indoxylic acid is readily converted into indoxyl, and this latter again into indigotin. On the other hand, with regard to the indirubin, its presence can only have originated from the simultaneous production of both indoxyl and isatin, and the question arises as to whether the isatin has been derived from the direct oxidation of indoxyl, or rather of indoxylic acid itself.

That indoxyl can be converted into isatin without an intermediate formation of indigotin has been shown by the Badische Anilin- & Soda-Fabrik (D.R.-P. 107719 of 1898) to be the case, and although air is not included among the reagents they employ, it is evident, and has been discussed in preceding communications, that the formation of indirubin during the manufacture of natural indigo can only be due to the previous production of isatin by the aerial oxidation of the indoxyl.

The quantity of indirubin, however, which can be obtained from indoxyl in this latter manner, even under the best known conditions, is but small in proportion to the indigotin which is simultaneously produced. Thus natural indigos are to be found which contain as high as from 8 to 10 per cent. of indirubin, and certain rare cases are on record in which even larger amounts have been detected, but these quantities are trifling when compared with the quantity (70 per cent.) of indirubin which was found in the colouring matter present in the indoxylic acid product under discussion.

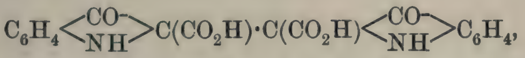
There is every reason to suppose that when indoxyl is oxidised by air it is preferably converted into indigotin, and it accordingly seems certain that the indoxylic acid itself has been the direct source of the isatin necessary for the indirubin condensation which took place in the sample.*

If the constitution of ψ-indoxylic acid is considered,



$$\mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{CH\cdot CO_2H},$$

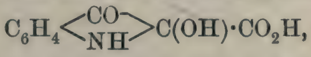
it is, of course, possible that on oxidation by air it might yield the acid,



$$\mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{C(CO_2H)\cdot C(CO_2H)}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{C_6H_4},$$

which by elimination of carbon dioxide and a further oxidation would be converted into indigotin.

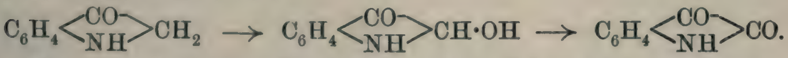
If, on the other hand, we suppose that the first product of the oxidation of the indoxylic acid is 2-hydroxy-ψ-indoxylic acid,



$$\mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{C(OH)\cdot CO_2H},$$

then it is easy to see that this cannot give indigotin by oxidation, but will yield isatin with elimination of carbon dioxide.

It is evident, also, that the conversion of ψ-indoxyl itself into ψ-isatin, according to the methods described by the Badische Anilin- & Soda-Fabrik (*loc. cit.*), or by the change which occurs to a small extent during the oxidation of indoxyl solutions by air, and is represented by the presence of indirubin in the indigo produced, can be similarly formulated :



$$\mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{CH_2} \longrightarrow \mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{CH\cdot OH} \longrightarrow \mathrm{C_6H_4}{<}\substack{\mathrm{CO}\\ \mathrm{NH}}{>}\mathrm{CO}.$$

From experiments on the aerial oxidation of a solution of indoxylic acid, described in the preceding paper (p. 842), there would appear to be some evidence that indigotin is not a product of this reaction.

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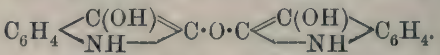
* It is considered that this oxidation has been due to the gradual admission of air to the samples. The investigation has yielded no evidence of the presence in the mixture of a substance known to behave as an oxidising agent, although, had this been the case, the main argument would not be affected.

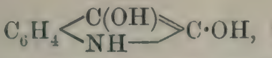
Thus it was observed that when a solution containing both indoxyl and indoxylic acid was oxidised by air in the presence of a small quantity of ammonia, both compounds yielded indigotin. On the other hand, in the absence of ammonia a much smaller yield of colouring matter was produced, and there could be no doubt that this small quantity had been derived mainly, if not entirely, from the indoxyl present. When the indigo had ceased to separate, addition of ammonia and shaking with air failed to increase the amount, showing that there was no indoxylic acid present, but, instead, a deep brown solution was obtained, due to the presence of brown matter and probably also of isatin. Unfortunately, at that time the necessity for a more detailed study of the reaction did not suggest itself.

The formation of a brown substance by the oxidation of an aqueous solution of indoxylic acid is very interesting, especially when taken in conjunction with the isolation of a brown compound from the decomposition products of "indophor" (*A* and *B*) described in this paper, and which so closely resembles the main constituent of indigo-brown, for if, as is suspected, this material is identical with that present in natural indigo, the origin of its presence in the dyestuff may be easily conjectured. There is no evidence that the leaves of *indigoferae* contain a glucoside of indoxylic acid, but, on the other hand, it is quite possible that indoxylic acid might be produced from indoxyl during the fermentation of the leaf extract. During this process a very large quantity of carbon dioxide is evolved, by means of which a portion of the indoxyl may be converted into the acid, and from this by subsequent oxidation the brown compound would be produced. In connexion with this point the statement of Rawson (*Report on the cultivation and manufacture of indigo.* Mozufferpore. 1904, 86) is interesting: "the blower . . . . by getting rid of carbon dioxide . . . . prevents decomposition of the colouring matter into worthless brown substances, which takes place to a greater extent under other conditions."

To account for the production of brown compounds from indoxylic acid, the following reactions suggest themselves as possible, taking into account the fact that the formula $C_{16}H_{12}O_3N_2$, which has been provisionally assigned to the main constituent of indigo-brown, contains more hydrogen and oxygen than indigotin itself. Briefly, it is considered that if, as discussed above, the first product of the oxidation of indoxylic acid is 2-hydroxyindoxylic acid, two molecules of the latter may condense with elimination of water, carbon dioxide being subsequently evolved. The substance thus obtained would possess the following formula:



$$C_6H_4{<}\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}{>}C\cdot O\cdot C{<}\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}{>}C_6H_4.$$

Again, if indoxyl on oxidation is in part converted into the compound  $C_6H_4{<}\substack{C(OH)\\NH-}{>}C\cdot OH$, the same product would naturally be obtained by such a condensation, and it is suggested that the secondary reaction which was observed to take place when the indoxyl solution derived from indican (see preceding paper) was oxidised by air is due either to this or some change of a similar nature.

Addendum.—Since the communication of this paper, a third sample of the "indophor" has been available for examination, and for this I am indebted to the kindness of Prof. W. Gardner, of Bradford. A qualitative investigation of this specimen which had been preserved in the museum of the Bradford Technical College since November, 1897, showed that it had undergone a similar alteration to that observed in the case of the specimens (*A* and *B*) above discussed. Thus, whereas it consisted mainly of indirubin, there was also present indigotin, the brown alkali soluble product, and a trace of indoxylic acid. There can thus be no doubt that the decomposition of indoxylic acid in these circumstances is characteristic of the substance.

CLOTHWORKERS' RESEARCH LABORATORY,
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XCIV.—*The Distillation of Butter Fat, Cocoanut Oil, and their Fatty Acids.*

By KENNETH SOMERVILLE CALDWELL and WILLIAM HOLDSWORTH HURTLEY.

CHEVREUL (*Les Corps Gras.*, pp. 23, 77, 178, 186) first showed that the fats and higher fatty acids could be distilled without decomposition in a Toricellian vacuum. He placed half a gram of the fat or fatty acid in the end of a barometer tube bent into the form of a retort, and showed that they volatilised without any change in composition; only in the case of stearic acid did he sometimes observe a slight yellow coloration.

The next to distil fats and fatty acids in a high vacuum was F. Krafft (Krafft and Weilandt, *Ber.*, 1896, **29**, 1316). For the production of a high vacuum he and his fellow workers usually employed a continuously acting water-mercury pump, and to test the vacuum a Crookes tube was placed between the receiver and pump.

We began the distillation of fats and fatty acids in a high vacuum with the object of ascertaining what glycerides are contained in various natural fats. Apart from the importance of such knowledge in biochemistry, it would obviously have great value in the analysis of butter and butter substitutes.

In our work we used a Gaede pump to obtain the necessary vacuum, and, following Krafft, we introduced a Crookes tube between receiver and pump.

In the course of our investigations, we had occasion to distil several of the fatty acids which Krafft had already distilled, and, owing to the very marked differences between his "boiling points" and ours, it is necessary to give precise details of the method of working. Krafft and Weilandt used an ordinary distilling flask of only 15 c.c. capacity: their thermometer was placed 20—30 mm. above the liquid, and they had a column of vapour of 25—30 mm. between the bulb of the thermometer and side-tube, and a further column of 35—40 mm. of vapour above the side-tube. They used a bath of fusible metal, the level of the metal being just below that of the substance in the flask. From 3 to 4 grams of substance were taken, and the experiment was stopped when about 1 gram of the substance remained in the distilling flask.

In our work we employed flasks of from 50 to 300 c.c. capacity, according to the amount of material we had to distil. With ordinary distilling flasks, distillation is very slow, owing to the greater part of the vapour condensing on the neck of the flask and trickling back into the bulb; we have always worked therefore with flasks having a trap in the neck and side-tube leading from the trap. Fats were distilled in 50 c.c. flasks having the trap about 2 cm. above the bulb, but fatty acids were distilled in flasks having the trap 6 cm. above the bulb. In all cases the thermometer bulb was, as is usual, level with the side-tube. To prevent the vapour of fatty acids reaching the rubber cork of the flasks, the necks were made very long. For fats a bath of fusible metal was employed, and for fatty acids one of paraffin. All our distillations were conducted in the vacuum of the cathode light.

On distilling the acids from cocoanut oil, we obtained large quantities of a product passing over at about 90°; this substance was lauric acid, the boiling point of which is, according to Krafft, 101°. We therefore determined the temperature at which the following fatty acids (obtained from Kahlbaum) distilled in our apparatus: lauric, myristic, palmitic, stearic, and oleic. The subjoined table gives our results and those of Krafft side by side:

	Krafft.	C. and H.		
Lauric acid *	101°	89°	with bath at	100°
Myristic acid	121—122°	98	,, ,,	130
Palmitic ,, *	138—139	114	,, ,,	140
Stearic ,,	154·4—155·5	128	,, ,,	160
Oleic ,,	153	130	,, ,,	160

(Krafft does not give the temperature of the bath.)

* In a paper by F. Krafft and Paul Lehmann (*Ber.*, 1905, **38**, 242), the boiling points of these acids, determined with the thermometer bulb level with the side-tube, are given as follows:

	Bath.	B. p.
Lauric acid	?	88—89°
Palmitic acid	205°	127—128°

To start a distillation a higher bath-temperature is required than that given in the table: this may be due to temperature equilibrium not being reached or to resistance to change of phase.

We offer the following explanation of these remarkable differences. On watching the distillation of these substances, it is seen that there is no boiling; the liquids remain perfectly quiet, but give off vapour at a rate and at a temperature which for any particular substance depends on the temperature of the bath. In distilling the pure acids, we worked at the rate of about 6 drops of distillate per minute as nearly as we could estimate, allowing for the difficulty of keeping the acids liquid until they reached the receiver. In carrying out a fractionation we have usually worked more slowly than this. All the above acids could be distilled at a lower temperature than those given in the table if the distillation were conducted more slowly.*

Krafft calls the numbers given under his name in the above table "boiling points," and he obtained them by working under the conditions described above. On the assumption that liquids have definite boiling points in a cathode vacuum, Krafft draws certain conclusions as to a relationship between the molecular weights of allied substances and their boiling points under a vapour column of a definite length. We believe that in the vacuum of the cathode light a liquid has no boiling point, but that it sublimes or evaporates, just as water does in air below its boiling point, at a rate and at a temperature depending on the nature of the substance and on the temperature to which it is heated.

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* In a paper in the current *Berichte* (Hansen and Krafft, *Ber.*, 1909, **42**, 210), which we did not see until our paper was completed, it is shown that lauric, myristic, palmitic, and stearic acids sublime at a measurable rate at such low temperatures as 22°, 27°, 32°, and 38° respectively; for example, lauric acid at 22° gave 0·82 gram in six hours.

Distillation of Butter Fat.

Butter is generally believed to contain tributyrin. With the idea of isolating this substance and probably other definite glycerides, we distilled samples of butter fat, prepared in the ordinary way, in the vacuum of the cathode light. Trilaurin from laurel oil, trimyristin from nutmeg butter, and tripalmitin appear to be the only fats distilled by Krafft. He gives the following "boiling points":

Trilaurin	260—275°
Trimyristin	290—300
Tripalmitin	310–320

For our own guidance, we attempted to distil tributyrin, tripalmitin, tristearin, and triolein.

Tributyrin, under a pressure of 1 mm. and at the ordinary temperature, appears to boil vigorously for a short time; this phenomenon, which is shown by all other fats and was observed by Chevreul, we believe to be due to the escape of dissolved air or oxygen, and possibly to hygroscopic moisture. In a good cathode vacuum, tributyrin sublimes rapidly, without the slightest sign of boiling, with the bath at 127° and the inner thermometer at 107°. It can be distilled, but more slowly, at 98°. To show that no decomposition had occurred, we saponified some of the residue and some of the distillate, and obtained the following figures:

1 gram residue required 9·7 c.c. *N*-sodium hydroxide.
1 ,, distillate ,, 9·72 c.c. ,, ,,
1 ,, by theory ,, 9·73 ,, ,, ,,

Tripalmitin distils with the bath above 360° and the inner thermometer at 280°.

1 gram residue required 3·75 c.c. *N*-sodium hydroxide.
1 ,, distillate ,, 3·68 ,, ,, ,,
1 ,, by theory ,, 3·72 ,, ,, ,,

A specimen of tristearin appeared to begin to distil with the bath at 273° and inner thermometer at 103°: the distillation then stopped. The distillate proved to be free stearic acid. On attempting to continue the distillation, the liquid bumped so badly that we could not determine the boiling point. In the case of triolein, a large quantity of gas escaped on working the mercury pump, and there was much frothing at the room temperature. With the bath at 260° and the inner thermometer at 135°, some free oleic acid distilled over, the distillation of the triolein beginning with the bath at 350° and the inner thermometer at 230°, but no constant temperature of the inner thermometer was observed.

The following iodine numbers were obtained:

Residue, 72·1. Distillate, 74·7. Theory, 86·2.

The triolein was therefore far from pure. The above glycerides were obtained from Kahlbaum.

Butter fat begins to distil with the bath at 260° and inner thermometer at 190°. For a first fraction, all that could be distilled up to 250° was taken. This fraction was liquid at room temperature, had a pale yellow colour, and a feeble taste not particularly like that of butter, but no taste at all resembling that of tributyrin, which is intensely bitter and disagreeable. The first fraction from each of our three specimens was redistilled. From our third specimen we distilled a second fraction up to 292°.

On the various distillates and residues we determined:

(1) The number of c.c. of *N*-sodium hydroxide required to saponify 1 gram of substance.

(2) The Reichert-Wollny number (the number of c.c. of *N*/10-sodium hydroxide required to neutralise the soluble and volatile fatty acids in 5 grams of the substance).

(3) The iodine number in some cases.

The results are given in the table:

		c.c. *N*-NaOH/gram.	Reichert-Wollny number.	Iodine number.
I. *Commercial Sample:*				
Distillate up to 250°	Distillate	4·61	48·0	—
	Residue	4·21	30·7	—
Distillate redistilled	Distillate	4·91	73·6	—
	Residue	3·98	28·9	—
II. *Pure Butter—Summer:*				
Distillate up to 250° (26 grams from 50 grams)	Distillate	4·46	50·9	—
	Residue	3·65	8·4	—
Distillate redistilled to 210°, 2/3 distilled over	Distillate	4·73	67·1	—
	Residue	4·12	24·9	—
III. *Pure Butter—Winter:*				
Distillate up to 250° (19 grams from 50 grams)	Distillate	4·39	57·6	19·7
	Residue	—	—	—
Distillate redistilled, 1/6 only distilled	Distillate	4·82	78·0	—
	Residue	4·84	45·8	—
Second distillate up to 292°, 19 grams	Distillate	4·06	21·1	26·7
	Residue	3·81	5·0	23 1

Samples II and III.

This butter was from a herd of 125 cows, chiefly shorthorns, with some Jerseys and cross-bred Guernsey shorthorns. In summer the cows are kept in the pastures and receive a little Bombay and linseed oil cake, bran, and oats; in winter they are fed on mangolds, hay, brewers' grains, an equal amount of the same oil-cakes, and bran.

On comparing our most volatile fraction with tributyrin, we have the following results:

Lowest butter fraction.	Tributyrin.
Distils slowly with bath at 250—270°.	Distils rapidly with bath at 127°.
Saponification number, 4·82.	Saponification number, 9·93.
Reichert-Wollny number, 78·0.	Reichert-Wollny number, 496·7.
Not unpleasant taste.	Extremely unpleasant taste.

We conclude from these results that there is no tributyrin in butter fat.

It has hitherto been supposed that tributyrin occurs to the extent of 5 to 7 per cent. in butter.

In specimen III, where the iodine numbers are given for the first distillate up to 250°, for the second distillate 250° to 292°, and for the residue, there is considerable iodine absorption in each; but none of the three gives an iodine number near that of triolein, 86·2. The glyceride oleostearopalmitin would have an iodine number 29·5. It seems probable, therefore, that there is little or no triolein in butter fat, but that the oleic acid is distributed among a considerable number of the butter glycerides present, most of it occurring as oleostearopalmitin.

Lewkowitsch has pointed out that improvements in the methods of analysis of butter fat have been accompanied step by step by improved methods of adulteration, and he draws attention to a patent taken out for the preparation of dibutyrostearin. This substance would have a Reichert-Wollny number of 200·8, and would distil over in the first fraction, thereby raising the Reichert-Wollny number of this fraction very considerably.

We have also distilled cocoanut oil, with the result summarised below:

Weight of cocoanut oil taken, 46 grams.

	c.c. *N*-NaOH/gram.	Reichert-Wollny.
Original	4·65	8·54
Distillate up to 210° (22 grams) ...	4·97	8·67
Residue	4·38	4·36

The Fatty Acids from Butter.

The butter (450 grams) was saponified by aqueous-alcoholic potash, the alcohol being finally distilled off by heating in an open basin. The solution of soaps was poured slowly into an excess of dilute sulphuric acid with shaking, and the whole distilled in steam. The non-volatile and volatile parts were dissolved separately in ether, dried over anhydrous sodium sulphate, and after removal of the ether were separately distilled.

Acids Volatile in Steam.

		Pressure in mm.	Bath.	B. p.*	Mol. wt.	M. p.	B. p. (760 mm.).
Distillates		44	115°	95°	104·3	—	—
		0	75	55—60	116·0	5°	196°
Residue		—	—	—	186·4	—	—

* By b. p. we mean always the temperature indicated by the inner thermometer during distillation.

Butyric acid, mol. wt. = 88 ; Hexoic acid, mol. wt. = 116. M. p. − 1·5°. B. p. 205°/760 mm.

Acids Not Volatile in Steam.

	Pressure in mm.	Bath.	B. p.	Distillate. Mol. wt.	Distillate. M. p.	Iodine number.
1st fraction ...	0	155°	133°	263·1	45·0°	27·1
2nd ,, ..	0	155	128—132°	260·3	45·0	
3rd ,, ...	0	165	128—135	279·2	49·0	40·1
4th ,, ...	0	250	175	283·4	53·5	36·4

Redistillation of united fractions (1) and (2):

1 (*a*) fraction	0	145°	122°	259·4	47°

As shown from the iodine numbers, all the above contain large quantities of oleic acid (iodine number, 90).

Fraction 1 (*a*) once recrystallised from acetic acid gave mol. wt. 255, m. p. 60—61°; it absorbed no iodine. (Palmitic acid, mol. wt. 256, m. p. 62·6.)

Fractions 3 and 4 recrystallised from acetic acid gave pure stearic acid, m. p. 69°.

The residue from distillate 4 (about 2 grams) was brown, soft, and was largely composed of cholesterin.

It will be seen from the above that by this method of distillation a good separation of the butter acids can be effected, and we are attempting the determination of the relative proportions of the butter fatty acids.

The Fatty Acids from Cocoanut Oil (419 *grams*).

These acids were obtained in the same way as the butter acids except that the soaps were extracted with ether to remove unsaponifiable matter, and instead of distilling in a current of steam the whole of the acids were dissolved together in ether.

At 20 mm. pressure and the temperature of the bath at 100°, we obtained 3 c.c. of distillate, which was not further examined. The residue was distilled in the vacuum of the cathode light. Owing to the presence of fatty acids of intermediate molecular weight, the fractionation was much more difficult. In all, we made thirty-six distillations, as the result of which the following fractions were obtained:

	Bath.	B. p.	Mol. wt.	M. p.		Mol. wt.	M. p.
1	70°	60°	150	12·5°	Octoic acid, $C_8H_{16}O_2$	144	16·5°
2	90	80	180	22·5	Decoic acid, $C_{10}H_{20}O_2$	172	31·3
3	100	90	200	42·0	Lauric acid, $C_{12}H_{24}O_2$	200	43·6
4	135	100	231	50·0	Myristic acid, $C_{14}H_{28}O_2$	228	53·8
5*	155	120	260	60·0	Palmitic acid, $C_{16}H_{32}O_2$	256	62·6
6	A distillate containing stearic and oleic acids.						

* As it contained a little oleic acid, this fraction was crystallised from acetic acid. All the other numbers relate to the fractions just as they were obtained on distillation.

The lauric acid is by far the largest constituent of the cocoanut oil acids, forming at least 60 per cent. of them. Ulzer (*Chem. Rev. Fett. Harz. Ind.*, 1899, **6**, 203) doubts the occurrence of palmitic acid; but we obtained several grams of pure palmitic acid from this oil.

Comparison of Butter and Cocoanut Oil as regards the Insoluble Fatty Acids.

Butter contains exceedingly little lauric acid—from a pound of butter we did not obtain any; cocoanut oil contains a large quantity—at the very least 60 per cent. of the total fatty acids. As the methods of analysis at present in use fail to detect with any certainty an adulteration of butter fat with 10 or, in the case of a good butter, even 20 per cent. of cocoanut oil, we distilled the insoluble fatty acids from:

(1) 100 grams of butter fat;

(2) 100 grams of cocoanut oil;

(3) 100 grams of a mixture of 10 grams of cocoanut oil with 90 grams of butter fat;

with the following results:

Butter Acids.

	Bath.	B. p.	Distillate.
Fraction 1...	90—100°	44°	Liquid, about 0·2 gram in three hours

No further distillation occurred until:

Fraction 2...	155—175°	125—131°	Solid, mol. wt. = 266·6 ; 78 grams

Residue: about 1·5 grams, very rich in cholesterin.

Cocoanut Oil Acids.

	Bath.	B. p.	Distillate.
Fraction 1......	105—131°	92—92·5°	Solid ; mol. wt. = 196·2 ; 62·1 grams
,, 2......	135°	105—108	,, ,, = 246·0 } 23·0 ,,
,, 3......	158	128°	,, ,, = 287·0

Very small residue.

Acids from Mixture of 10 *grams of Cocoanut Oil and* 90 *grams of Butter Fat.*

	Bath.	B. p.	Distillate.
Fraction 1	110—141°	80—113·5°	Solid ; 13 grams.

Not further distilled.

The 13 grams of distillate were slowly fractionated:

	Bath.	B. p.	Mol. wt.	M. p.	Solidified.	Distillate, grams.
Fraction 1 ...	79—100°	52—73°	150	0·0°	—	3·0
,, 2 ...	100—101	to 79°	183	11·0	—	1·6
,, 3 ...	100—106	at 79	196	39·0	34°	1·6
,, 4 ...	106—109	to 83	203	42·5	38	3·0
,, 5 ...	118—128	to 95	221	44·0	41	2·1

Fractions 3 and 4 are nearly pure lauric acid. The following table shows what a great difference is produced in the temperature at which the insoluble fatty acids begin to distil when butter fat is mixed with cocoanut oil:

Insoluble acids from	Bath.	B. p.	Weight of distillate, grams.
100 grams of butter fat	to 141°	—	0
100 ,, cocoanut oil	,, 131	92—92·5	62
90 ,, butter fat + 10 grams of cocoanut oil.....................	,, 141	80—113·5	13

By this method, therefore, it is possible to detect with certainty quite small adulterations of butter with cocoanut oil.

We are at present engaged in applying this method to the quantitative estimation of the fatty acids in various fats, to the isolation of definite glycerides, and to the working out of certain other questions which have presented themselves to us in the course of this work.

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XCV.—*The Preparation and Properties of the* N-*Tribromo-substituted Hydrazines* (*the Diazonium Perbromides*).

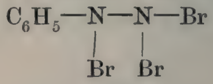
By Frederick Daniel Chattaway.

The diazonium perbromides, although easily prepared, stable, and safe to handle, have not proved useful in chemical investigation or technical processes, and have in consequence been little studied. They were among the first derivatives of the diazo-compounds to be discovered, and Griess, in an early paper, described the preparation and properties of a considerable number (*Phil. Trans.*, 1864, **154**, 667). Griess assigned the formula $C_6H_4N_2HBr,Br_2$ to diazobenzene perbromide, and stated that its constitution seemed the same as that of the periodide of tetraethylammonium and similar compounds of other bases.

In the second volume of his text-book of organic chemistry, published in 1866, Kekulé wrote that diazobenzene perbromide could be regarded either as a true perbromide, that is, as an additive compound formed by the union of a molecule of bromine with a molecule of diazobenzene bromide, a conception which he represented by the formula (I), or as a compound in which the

$$C_6H_5{-}N{=}N{-}Br{\cdot}Br_2$$

(I.)

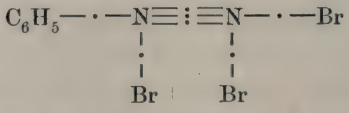


$$\begin{array}{lll} C_6H_5{-} & N{-} & N{-}Br \\ & | & | \\ & Br & Br \end{array}$$

(II.)

two nitrogen atoms of diazobenzene bromide were linked by a single unit of affinity, and each was further united with an atom of bromine. This idea he expressed by the formula (II), but added that the behaviour of the compound, and especially the circumstance that when washed with ether it lost bromine and reverted to diazobenzene bromide, pointed to the former view as being the more correct one.

Erlenmeyer, in a theoretical paper on the constitution of the diazo-compounds (*Ber.*, 1874, **7**, 1111), without giving any reasons, ascribed to the compound the constitution:



$$\begin{array}{lcccl} C_6H_5{-}\cdot{-} & N & \equiv\vdots\equiv & N & {-}\cdot{-}Br \\ & \vdots & & \vdots & \\ & Br & & Br & \end{array}$$

Erlenmeyer's view, which is in effect * that the diazo-perbromides should be regarded as *N*-tribromo-substitution products of the hydrazines, was generally accepted * up to about thirteen years ago, when Hantzsch (*Ber.*, 1895, **28**, 2755) put forward the suggestion, scarcely to be distinguished from the original one of Griess or from Kekulé's view, that they and the other perhalides discovered by him must be regarded as diazonium perhalides having the general formula

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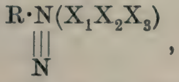
* Whether the two nitrogen atoms are represented in the formula as united by three strokes or by one, or by six strokes and three dots, there is no essential difference of conception, which is, that the nitrogens are linked together by whatever affinity they possess after satisfying the affinities of the groups otherwise attached to them.



$$R\cdot\underset{\underset{\displaystyle N}{|||}}{N}(X_1X_2X_3) ,$$

and constituted similarly to the trihalides of the alkali metals and of the substituted ammonium residues. Hantzsch's suggestion is the outcome of his views on the constitution of diazonium compounds, and practically receives support only from the easy decomposition of these compounds into diazonium salts and free halogen, referred to by Kekulé, whilst it immensely complicates the explanation of other reactions, notably that of ammonia, on these compounds, whereby the diazoimides are produced, a reaction very simply explained by the hydrazine formula.

The circumstance that structural isomerism among the mixed perhalides has not been observed cannot be regarded as an argument in favour of either view, as it can never be asserted with certainty in any particular case that rearrangement into the most stable form has not occurred, or even that the slight differences in properties which might be supposed to exist in such compounds could be recognised.

The formation of unstable higher bromine additive products when the diazo-perbromides are brought into contact with free bromine, and of diazoimides when they react with ammonia, are arguments against Hantzsch's suggestion.

The view rejected by Kekulé and later adopted by Erlenmeyer, that the diazonium perbromides have the constitution $R\cdot NBr\cdot NBr_2$, that is, are *N*-tribromo-derivatives of the aromatic hydrazines, receives strong support from the fact that they are produced quantitatively when the requisite amounts of bromine are added to aromatic hydrazines dissolved in acetic acid.

The author has recently shown (Trans., 1908, **93**, 852) that diazonium bromides are produced quantitatively by the action of bromine on the aromatic hydrazines, and has expressed the view that these compounds, when in acid solution, are really *N*-dibromo-substituted hydrazines produced by a process of substitution exactly similar to that which occurs when other compounds containing hydrogen attached to nitrogen are submitted to the action of bromine.

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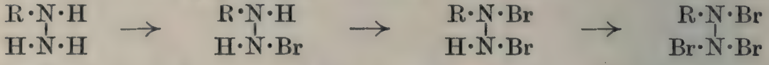
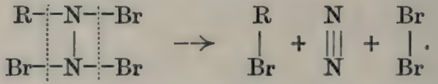
* Bamberger (*Ber.*, 1894, **27**, 1273) definitely formulates diazobenzene perbromide as tribromophenylhydrazine, and this view of its constitution underlies his use of it for the preparation of nitrosobenzene.

According to this view the production of diazo-perbromides is the final and completing step in the replacement of the hydrogen of the $\cdot NH\cdot NH_2$ group by bromine, thus:



$$\begin{array}{c}\mathrm{R\cdot N\cdot H}\\ |\\ \mathrm{H\cdot N\cdot H}\end{array} \longrightarrow \begin{array}{c}\mathrm{R\cdot N\cdot H}\\ |\\ \mathrm{H\cdot N\cdot Br}\end{array} \longrightarrow \begin{array}{c}\mathrm{R\cdot N\cdot Br}\\ |\\ \mathrm{H\cdot N\cdot Br}\end{array} \longrightarrow \begin{array}{c}\mathrm{R\cdot N\cdot Br}\\ |\\ \mathrm{Br\cdot N\cdot Br}\end{array}$$

The entire behaviour of the diazonium perbromides is in accord with this view of their constitution; for example, they are in exactly the condition necessary for the typical diazo-composition to take place; this, in fact, occurs when they are heated alone or suspended either in chloroform or glacial acetic acid:



$$\begin{array}{c}\mathrm{R-N-Br}\\ |\\ \mathrm{Br-N-Br}\end{array} \longrightarrow \begin{array}{c}\mathrm{R}\\ |\\ \mathrm{Br}\end{array} + \begin{array}{c}\mathrm{N}\\ |||\\ \mathrm{N}\end{array} + \begin{array}{c}\mathrm{Br}\\ |\\ \mathrm{Br}\end{array}.$$

All the diazo-perbromides, when brought into contact with free bromine, combine with it to form unstable compounds, in which the halogen is held much as water is in a crystalline hydrated salt. These unstable compounds are to be regarded as perbromides, the bromine in them being much less firmly attached to the other atoms composing the molecule than the bromine replacing hydrogen attached to tervalent nitrogen in the hydrazines. These bromine additive compounds are only stable under a considerable pressure of bromine vapour, and consequently lose bromine and leave behind the parent substances when washed with ether or exposed in the air or in a vacuum.

It would be well, therefore, to abandon the use of the term diazo- or diazonium perbromides for the *N*-substituted hydrazines, and to style them, in accordance with their constitution, *N*-tribromohydrazines, using the designation *N*-tribromohydrazine perbromides for the less stable compounds formed by the union of bromine with them.

Preparation of N-*Tribromo-substitution Derivatives from Aromatic Hydrazines.*

The preparation of *N*-tribromophenylhydrazine only is described, as all other derivatives of the kind can be obtained in a precisely similar manner from the corresponding hydrazines. Six grams of freshly distilled phenylhydrazine were dissolved in 10 c.c. of glacial acetic acid, and 20 grams of crushed ice were added. 9·6 Grams of bromine were similarly dissolved in 10 c.c. of glacial acetic acid, and 20 grams of crushed ice added. When the temperature of each solution had fallen to about −15°, the phenylhydrazine solution was quickly added to the bromine solution, the latter being vigorously stirred during the process. Although on adding the hydrazine a slight local deposition of solid occurred, this re-dissolved, and when all the hydrazine had been added a clear solution was obtained, from which almost immediately orange-yellow plates of *N*-tribromophenylhydrazine separated, the liquid becoming a pulp of crystals. After collecting, washing with dry chloroform, and drying over phosphoric oxide, 6·5 grams were obtained, this being 94 per cent. of the theoretical yield (6·9 grams).

Preparation of N-*Tribromophenylhydrazine from Benzenediazonium Bromide.*

All writers who have described the interaction between benzenediazonium bromide and bromine, either alone or dissolved in an aqueous solution of potassium bromide, have stated that a brownish-red oil first separates, which solidifies to a crystalline mass only after it has been separated from the mother liquor and either washed with ether or exposed for some time to the air [compare Griess (*Phil. Trans.*, 1864, **157**, 667), Saunders (*Amer. Chem. J.*, 1891, **13**, 486), Bamberger (*Ber.*, 1894, **27**, 1273)]. This red, oily liquid is an additive product of *N*-tribromophenylhydrazine and bromine, probably $C_6H_5\cdot NBr_3\cdot NBr_6$, the dissociation pressure of which at the ordinary temperature is considerable. Its formation can be avoided if the solution of bromine is added very cautiously to the solution of the diazonium salt, so that it is nowhere present in any excess. If bromine itself, and not a solution in aqueous potassium bromide, is added, the drops, on falling into the solution of the diazonium salt, form pasty masses of the additive product, which only disintegrate and lose the excess of bromine on very vigorous shaking with some slight excess of the diazonium salt. This oily, additive product is formed whenever bromine is brought into contact with *N*-tribromophenylhydrazine, whether the dry solid is exposed to the vapour of bromine or brought into contact with it suspended in water or dissolved in chloroform or glacial acetic acid. When *N*-tribromophenylhydrazine is placed in water it is dissociated to some extent into free bromine and diazonium bromide; the former then combines with the unchanged *N*-tribrcmo-derivative to form the liquid additive product. The interaction between diazonium bromide and bromine is therefore a reversible change, and the *N*-tribromophenylhydrazine can only be obtained free from the oily additive compound if some excess of diazonium bromide is present.

Stability of Dry N-*Tribromophenylhydrazine.*

Two grams of *N*-tribromophenylhydrazine, dried thoroughly over phosphoric oxide, were spread in a thin layer on a watch-glass and exposed over freshly-burnt lime and solid potassium hydroxide in a vacuum desiccator at the lowest pressure obtainable by a water-pump. Each day for a month it was weighed. It was found to lose weight regularly but very slowly, the loss never exceeding 0·001 gram in twenty-four hours. This loss in weight was found to be due to a slow decomposition into benzenediazonium bromide and bromine, the latter being absorbed as soon as it was liberated by the lime, the former accumulating in the solid.

Decomposition of N-*Tribromophenylhydrazine when Exposed to Moist Air.*

A quantity of *N*-tribromophenylhydrazine was exposed in a thin layer freely to the air. It soon became white and damp round the edges, and in a few days had changed into a moist, yellowish-white solid. After about a week, the yellow colour had completely disappeared, and a semi-liquid mass containing a little of a white solid and slowly giving off gas was left. The solid was collected, and proved to be 2 : 4 : 6-tribromophenol; the liquid was benzenediazonium bromide in a deliquesced state. From the latter, pale yellow, glistening plates of benzenediazonium bromide separated on adding alcohol, and then excess of dry ether. These were washed with ether, dried, and analysed:

0·5747 gave 0·5838 AgBr. Br = 43·23.

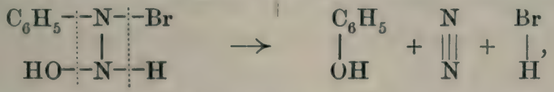
$C_6H_5N_2Br$ requires Br = 43·20 per cent.

A further portion was converted by means of β-naphthol into benzeneazo-β-naphthol, which was obtained perfectly pure on once crystallising from alcohol. An estimation of the amount yielded by a weighed quantity of the salt was made:

0·4833 gave 0·6452 $C_6H_5{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$. Theory requires 0·6480.

On being exposed to moist air, therefore, bromine is slowly given off as in a vacuum, and benzenediazonium bromide is formed; the latter deliquesces, and is partly converted by the absorbed water into phenol with escape of nitrogen. The phenol then reacts with the bromine liberated, still further hastening the dissociation and being itself converted into 2 : 4 : 6-tribromophenol, the most highly substituted derivative of phenol producible by direct bromination.

A similar action takes place when *N*-tribromophenylhydrazine is placed in water; at first a small quantity breaks down into benzenediazonium bromide and bromine; the latter partly remains dissolved, and partly combines with the unchanged *N*-tribromophenylhydrazine, which it converts into the liquid bromine additive product. On standing, the benzenediazonium bromide in combination with water undergoes the typical diazo-decomposition:



$$\begin{array}{c} C_6H_5-N-Br \\ | \\ HO-N-H \end{array} \longrightarrow \begin{array}{c} C_6H_5 \\ | \\ OH \end{array} + \begin{array}{c} N \\ ||| \\ N \end{array} + \begin{array}{c} Br \\ | \\ H \end{array},$$

yielding hydrogen bromide, nitrogen, and phenol; the phenol is then, as before, converted by the bromine present into 2 : 4 : 6-tribromophenol. These actions proceed until all the *N*-tribromoderivative has disappeared, 2 : 4 : 6-tribromophenol and benzenediazonium bromide being only produced, the further decomposition of the latter then giving rise to phenol.

A number of experiments were made to ascertain if bromine attached to nitrogen in *N*-tribromophenylhydrazine passed easily into the nucleus as it does when *N*-chloro- and *N*-bromo-anilides are transformed.

Action of Concentrated Hydrochloric Acid on N-*Tribromophenylhydrazine.*

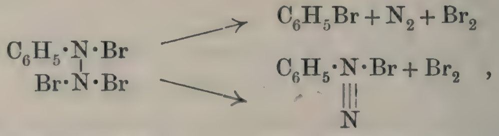
Finely-powdered *N*-tribromophenylhydrazine was suspended in ten times its weight of concentrated hydrochloric acid, and the mixture shaken for some time. An action similar to that which occurs when the compound is suspended in water took place. No gas was evolved, but the solid became pasty and settled to the bottom, whilst the liquid became coloured from dissolved free bromine. The pale brown liquid was decanted from the pasty solid, and air was drawn through it until the colour of bromine had completely disappeared. The liquid was then neutralised, and β-naphthol dissolved in potassium hydroxide added, when benzeneazo-β-naphthol was produced.

Action of Hydrogen Chloride on N-*Tribromophenylhydrazine Suspended in Acetic Acid or Alcohol.*

Gaseous hydrogen chloride was passed into a cooled mixture of *N*-tribromophenylhydrazine and five times its weight of glacial acetic acid until the liquid fumed strongly. Bromine was set free in the liquid, and a little gas was liberated. Some heat was developed, and the solid partly dissolved. The liquid was diluted with one-fifth of its bulk of concentrated hydrochloric acid, and the mixture kept at the ordinary temperature for two days until the free bromine and *N*-tribromo-substituted hydrazine had both disappeared and the colour of the liquid had become pale yellow. During this time a considerable quantity of gas had been liberated, bromobenzene had been produced, and a white deposit of 2:4:6-tribromophenol had separated. The liquid was then filtered, neutralised, and a solution of β-naphthol in potassium hydroxide added. Benzeneazo-β-naphthol, unaccompanied by any bromo-substituted azo-compound, was precipitated.

Decomposition of N-*Tribromophenylhydrazine by Alcohol.*

When *N*-tribromophenylhydrazine is suspended in alcohol at the ordinary temperature, action takes place very slowly, but after a week or thereabouts, depending on the temperature, the whole of the solid disappears and the liquid contains benzene, bromobenzene, ethyl bromide, 2:4:6-tribromophenol, and a little 2:4:6-tribromophenetole. In this action, therefore, the substituted hydrazine decomposes in two ways into bromine, nitrogen, and bromobenzene, and into bromine and benzenediazonium bromide, thus:



$$\begin{array}{c} C_6H_5\cdot\underset{|}{N}\cdot Br \\ Br\cdot N\cdot Br \end{array} \begin{array}{l} \nearrow\ C_6H_5Br + N_2 + Br_2 \\ \searrow\ C_6H_5\cdot\underset{\underset{N}{|||}}{N}\cdot Br + Br_2 \end{array},$$

the latter subsequently decomposing and yielding benzene, phenol, and phenetole, the free bromine reacting with these and also with the alcohol.

If a mixture of *N*-tribromophenylhydrazine and alcohol is cooled and saturated with hydrogen chloride, the temperature never being allowed to rise much above zero, little or no gas is evolved, the *N*-tribromo-substituted hydrazine disappears, and benzenediazonium chloride crystallises out, the bromine reacting with the alcohol.

If, instead of allowing the *N*-tribromophenylhydrazine suspended in alcohol slowly to decompose at the ordinary temperature, the mixture be heated until the temperature at which the typical diazo-decomposition commences is reached, violent action takes place, nitrogen is evolved in torrents, and bromobenzene and free bromine are formed; the latter as it is liberated reacts with the alcohol to form ethyl bromide, hydrogen bromide and acetaldehyde still further increasing the violence of the action. Only a small quantity of phenetole and its bromo-substitution products are formed.

Decomposition of N-*Tribromo-substituted Hydrazines by Heat.*

The decomposition of several of the *N*-tribromo-substituted hydrazines by heat was investigated by Griess, who heated them either mixed with sodium carbonate or suspended in alcohol.

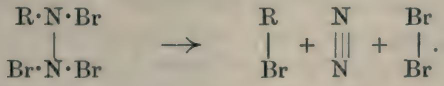
The decomposition is much more conveniently effected by heating the compounds, suspended in three to six times their weight of glacial acetic acid, in a flask which should be not more than one-twelfth filled by the liquid. Owing to the liberation of free bromine in the decomposition and to the almost violent disengagement of nitrogen and consequent frothing, the large flask in which the decomposition is effected must be connected with an efficient condenser attached to a receiver, which in its turn communicates with a second condenser and receiver and then with some arrangement for absorbing bromine.

On raising the temperature to 80—100°, the *N*-tribromo-substituted hydrazines wholly or partly dissolve, then nitrogen and bromine commence to be disengaged, and the action proceeds, with increasing rapidity and violent frothing, to completion without any further application of heat. A clear liquid is thus obtained coloured red by bromine, from which, after distilling off the bromine, the bromo-substituted benzenes or phenols formed separate on addition of water. The substituted phenols, if any are formed, can be extracted by alkali hydroxide, the substituted hydrocarbons being thus left practically pure. The decomposition of *N*-tribromophenylhydrazine thus yielded, besides nitrogen and bromine, monobromobenzene and a little 2 : 4 : 6-tribromophenol.

N-Tribromo-*p*-bromophenylhydrazine gave a practically theoretical yield of *p*-dibromobenzene. After distilling in a current of steam and crystallising from alcohol, a yield of 92 per cent. was obtained.

N-Tribromo-2 : 4-dibromophenylhydrazine and *N*-tribromo-2 : 4 : 6-tribromophenylhydrazine similarly decomposed yielded 1 : 2 : 4-tribromobenzene and 1 : 2 : 4 : 6-tetrabromobenzene respectively in theoretical amount.

All the *N*-tribromo-substituted hydrazines, therefore, when heated, undergo the typical diazo-decomposition:



$$\begin{array}{c} \mathrm{R\cdot N\cdot Br} \\ | \\ \mathrm{Br\cdot N\cdot Br} \end{array} \longrightarrow \begin{array}{c} \mathrm{R} \\ | \\ \mathrm{Br} \end{array} + \begin{array}{c} \mathrm{N} \\ ||| \\ \mathrm{N} \end{array} + \begin{array}{c} \mathrm{Br} \\ | \\ \mathrm{Br} \end{array}.$$

The *N*-tribromohydrazines can be similarly decomposed by heating them suspended in dry chloroform.

The same products are formed if the oily bromine additive products of the *N*-tribromohydrazines are thus decomposed, but the actions are not so smooth, small quantities of tarry matters being formed.

The thanks of the author are due to Professor Odling for placing a laboratory at his disposal, and to the Government Grant Committee of the Royal Society for a grant which has partly covered the cost of this investigation.

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Oxford.

XCVI.—*A Method for Investigating Dissociation Equilibria in Solutions, and its Application to the Study of Aqueous Potassium Mercuri-iodide Solutions.*

By Harry Medforth Dawson.

The object of this paper is to describe a method for the investigation of dissociation equilibria such as are frequently met with in the formation of complex acids, bases, and salts in aqueous solution. In the first instance, the general character of the method will be discussed, and its application will then be illustrated by experiments which have been made to determine the nature of aqueous solutions containing mercuric and potassium iodides.

The essential feature of the method to be described consists in the mode of determination of the proportion in which one of the two components of the solution is present in the uncombined condition. This is effected by adding to the solution a third substance which combines with this component to form another complex compound, for which the value of the dissociation constant is known. Under suitable conditions it is easily possible to avoid the complications which might be conceived to result from the competitive action of the chemical affinities which give rise to the two different complex compounds.

If the two components of the aqueous solution be denoted by A and B, and if these combine with the formation of a complex compound of the type A_mB_n, the relationship between the concentrations of the substances taking part in the equilibrium represented by the formula

$$mA + nB \rightleftharpoons A_mB_n$$

will be determined by a constant K_1, where

$$K_1 = \frac{[A]^m[B]^n}{[A_mB_n]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

If A is a strong electrolyte, the relationship between the components may be expressed in terms of ions, a complex ion resulting from the union of the weak electrolyte B with one of the ions of the component A.

The problem to be solved is the determination of the value of the ratio $m:n$. If, as presumed, a single complex electrolyte is formed, the value of m/n should remain constant when the concentrations of the components A and B undergo either relative or absolute variation.

Let C represent a third substance, which is of the nature of a weak electrolyte and which, like B, combines with A to form a complex electrolyte of the type A_pC_q, and suppose that a small quantity of C is added to a solution containing A and B. Corresponding with the equilibrium expressed by the formula

$$pA + qC \rightleftharpoons A_pC_q$$

the relationship between the concentrations of the reacting substances will be determined by a constant K_2, where

$$K_2 = \frac{[A]^p[C]^q}{[A_pC_q]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

If the total quantities of A, B, and C in unit-volume of the solution as well as the value of the dissociation constant K_2 are known, and if the fraction of C which is present in the free condition is determined, the concentration of uncombined A in the aqueous solution can be calculated from equation (2).

In the choice of the third substance C, which is to be utilised in the investigation of the complex substance or substances formed by the combination of A and B, it is not only necessary to know the value of the constant K_2, but C should be such that the amount of it present in the free state in the aqueous solutions can be measured with considerable accuracy. In general, this measurement will be most conveniently effected by means of distribution experiments. A liquid, immiscible with water, in which the weak electrolytes B and C are readily soluble, but which does not dissolve the strong electrolytes A, A_mB_n, and A_pC_q to any appreciable extent, can readily be found, and if the ratios of distribution of B and C between water and this solvent are known, the concentration of uncombined B and C in a given aqueous solution can be determined. Since the total concentration of C is known, that of the complex electrolyte A_pC_q is at once obtained, and from equation (2) the concentration of uncombined A in the solution can be calculated. Since, further, the total concentrations of A and B are known, the ratio in which A and B are combined in the form of the complex electrolyte A_mB_n can be deduced. If only one complex is formed by the union of A and B when the proportions of the components are subjected to considerable variation, the values so obtained for the concentration of free A, free B, and the complex A_mB_n ought to satisfy the equation (1).

As a special case, that in which the substance B is only very slightly soluble in water may be considered. In these circumstances the quantity of B which is present in the form of the complex A_mB_n is given by the total concentration of B, and if the quantities of A which are present in the free state and in the form of the complex A_pC_q are subtracted from the total quantity of A in the solution, the quantity of A present in the form of the complex A_mB_n is obtained. This gives us the molar ratio m/n of A to B in the complex substance under investigation.

The particular system to which the method of investigation described above has been applied, represents one which has already been studied by a number of workers, and various methods have been employed to ascertain the nature of the complex anions which are formed by the union of mercuric iodide with the simple iodine ions.

Abegg, Immerwahr, and Jander (*Zeitsch. Elektrochem.*, 1902, **8**, 688) measured the solubility of mercuric iodide in potassium iodide solutions of different concentrations; the data so obtained furnish evidence solely in regard to the nature of solutions saturated with mercuric iodide.

Sherrill (*Zeitsch. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103) examined the nature of the complex ions by measurements of the electromotive force of concentration cells of the type Hg | HgI_2 solution (1) || HgI_2 solution (2) | Hg, of the changes which take place in the freezing points of potassium iodide solutions on the addition of mercuric iodide, and by experiments on the distribution of mercuric iodide between benzene and potassium iodide solutions.

The measurements of Bredig and Walton (*Zeitsch. Elektrochem.*, 1903, **9**, 114; *Zeitsch. physikal. Chem.*, 1904, **47**, 185) of the catalytic influence of the iodides on the decomposition of hydrogen peroxide indicate that the velocity of decomposition is directly proportional to the concentration of the iodine ions. When, by the addition of mercuric iodide to a given potassium iodide solution, the concentration of the iodine ions is diminished in consequence of the formation of complex anions, the number of iodine ions rendered inactive can be calculated from the corresponding reduction in the catalytic activity of the solution. Reference will be made to the results of these investigations at the end of the paper.

In the experiments recorded here, the following procedure was adopted. A weighed quantity of mercuric iodide was dissolved in a measured volume of potassium iodide solution of determined concentration, and the resulting liquid was shaken at constant temperature with a solution of iodine in carefully purified carbon disulphide or carbon tetrachloride until a condition of equilibrium was reached. The concentration of the iodine in the two practically immiscible solutions was determined by means of thiosulphate solution, and from the measured value of the ratio of distribution of iodine between water and the organic solvent, the concentration of the free iodine in the aqueous solution was calculated. In the first experiments carried out at 15° ± 0·05°, carbon disulphide was used as the solvent for iodine; in the later experiments at 18° ± 0·02°, carbon tetrachloride was employed.

Suppose that

v = the volume of aqueous solution in litres which contains one mol. iodine (titrated by thiosulphate)

x = the fraction of the total iodine which is present in the free state

a and b = mols. potassium iodide and mercuric iodide respectively present in v litres of the solution,

and, further, that a single complex electrolyte is formed, which may be represented by the formula $m\mathrm{KI}, n\mathrm{HgI_2}$ or $\mathrm{HgI_2}, \frac{m}{n}\mathrm{KI}$. For the concentrations of the various components of the solution, we then obtain

Component of solution...	I_2	$\mathrm{HgI_2}, \frac{m}{n}\mathrm{KI}$	$\mathrm{KI_3}$	KI
Concentration	$\frac{x}{v}$	$\frac{b}{v}$	$\frac{1-x}{v}$	$\frac{a-\frac{m}{n}b-(1-x)}{v}$

According to Jakowkin, the equilibrium between iodine and potassium iodide in aqueous solutions, the concentrations of which do not exceed certain limits, is in exact agreement with the requirements of the law of mass action applied to the dissociation equation

$$\mathrm{KI_3} \rightleftarrows \mathrm{I} + \mathrm{I_2}.$$

With the above symbols, application of the mass action law leads to the equation:

$$k = \frac{x(a - \frac{m}{n}b - 1 + x)}{v(1-x)}.$$

Special experiments in which no mercuric iodide was present in the solutions used gave for k at 15° the value 0·001035, and at 18° the higher value, 0·001153. The dissociation constant having been determined, the above equation can be directly employed for the calculation of $\frac{m}{n}$, since all the other quantities involved—a, b, v, and x—are given by the experimental measurements.

A difference in the experiments with carbon disulphide and those with carbon tetrachloride is to be noted. This is due to the fact that, whilst mercuric iodide is only slightly soluble in the latter solvent, it dissolves fairly readily in carbon disulphide. Measurements of the solubility were made by shaking the liquids at constant temperature with a large excess of mercuric iodide for several hours and evaporating the solvent from a known volume of the solution at as low a temperature as possible in order to avoid volatilisation of the dissolved substance. As the mean result of two determinations, the saturated solution in carbon disulphide was found to contain 0·00688 mol. of mercuric iodide per litre (15°), and that in carbon tetrachloride, 0·000375 mol. per litre (18°). These numbers show that mercuric iodide is about twenty times more soluble in carbon disulphide than in carbon tetrachloride at the respective temperatures employed in the distribution experiments. As a consequence of the relatively large solubility of mercuric iodide in carbon disulphide, appreciable quantities of the mercury halide were found to be extracted by this solvent from the aqueous iodide solutions in the distribution experiments, whereas the quantities removed by carbon tetrachloride were, in general, negligibly small. It is evident from this that the distribution measurements with carbon disulphide not only permit of the determination of the uncombined potassium iodide in the aqueous solutions, but by estimating the concentration of the mercuric iodide in the carbon disulphide, that of the uncombined mercury halide in the aqueous solutions could also be obtained when the ratio of distribution of the substance between carbon disulphide and water is known. Although measurements of the mercuric iodide concentration in the carbon disulphide solution were made, the values obtained are not considered to be sufficiently accurate for the purpose of testing the validity of equation (1). They suffice, however, for the estimation of the change which takes place in the concentration of the mercuric iodide in the aqueous solutions when these are shaken with carbon disulphide, and have been used for this purpose.

In tables I and II are recorded the experimental data and the calculated results for several series of measurements. It may be observed that the concentration of the potassium iodide varies from 0·025 to 0·20 mol. per litre, these probably representing the limits of concentration for which accurate values of m/n can be obtained by the method described. For each solution of potassium iodide, the concentration of the mercuric iodide increases in the successive experiments. The first column gives the number of the experiment, the second the molar concentration of the mercuric iodide in the aqueous solution, the third and fourth the iodine concentrations in mols. per litre of the aqueous and carbon disulphide or carbon tetrachloride solutions respectively, the next four columns contain the calculated values of v, x, a, and b, which have the significance previously assigned to them, and in the last the ratio of the number of mols. of potassium iodide in combination with one mol. of mercuric iodide $\left(\frac{m}{n}\right)$ is recorded.

TABLE I.

Experiments with Carbon Disulphide (15°).

No.	HgI_2 (conc.).	I_2 conc. (aq.).	I_2 conc. (CS_2).	*v.*	*x.*	*a.*	*b.*	*m/n.*
0·05 *n*KI.								
1	0·003878	0·007693	0·1359	129·8	0·02848	6·49	0·5305	1·86
2	0·009802	0·006106	0·1427	163·6	0·03769	8·18	1·603	1·81
3	0·01410	0·004965	0·1467	201·1	0·04763	10·05	2·835	1·74
4	0·01919	0·003728	0·1517	267·9	0·06560	13·39	5·140	1·65
0·10 *n*KI.								
5	0·007518	0·008831	0·07288	113·2	0·01331	11·32	0·851	1·94
6	0·01477	0·007754	0·07575	128·8	0·01577	12·88	1·902	1·88
7	0·03850	0·004003	0·08726	249·5	0·03514	24·95	9·610	1·76
0·20 *n*KI.								
8	0·00903	0·01700	0·06540	58·75	0·006203	11·75	0·531	1·92
9	0·01827	0·01587	0·06775	62·94	0·006887	12·59	1·150	1·91
10	0·03495	0·01260	0·06592	79·27	0·008439	15·85	2·770	1·88
11	0·04311	0·01157	0·06790	86·30	0·009464	17·26	3·720	1·86
12	0·06648	0·008206	0·07482	121·7	0·01469	24·34	8·09	1·84
13	0·07348	0·007839	0·08370	127·5	0·01723	25·50	9·37	1·81

TABLE II.

Experiments with Carbon Tetrachloride (18°).

No.	HgI_2 (conc.).	I_2 conc. (aq.).	I_2 (conc.) (CS_2).	*v.*	*x.*	*a.*	*b.*	*m/n.*
0·025 *n*KI.								
14	0·002209	0·002248	0·01087	444·9	0·05845	11·12	0·983	1·95
15	0·004387	0·002072	0·01191	482·5	0·0939	12·06	2·12	1·73
16	0·008718	0·001605	0·01393	622·9	0·1048	15·57	5·43	1·57
0·05 *n*KI.								
17	0·00474	0·003861	0·009668	259·0	0·03024	12·95	1·228	1·95
18	0·01031	0·003353	0·01098	298·3	0·03958	14·91	3·075	1·82
19	0·01922	0·002334	0·01317	428·4	0·06814	21·42	8·235	1·66
0·1 *n*KI.								
20	0·009592	0·005888	0·007352	169·8	0·01508	16·98	1·629	1·97
21	0·04399	0·003263	0·01295	306·5	0·04793	30·65	13·48	1·68

Before proceeding to discuss the results of these experiments, reference should be made to two approximations which are involved in the calculation of the values of m/n.

In the first place, no account has been taken of the alteration in the distribution of the iodine which is brought about by the substances present in the aqueous solutions, the partition-coefficient obtained for the distribution of iodine between pure water and carbon disulphide or tetrachloride having been used in the case of all the solutions examined. The fact may, however, be recalled that, according to the distribution experiments of Jakowkin (*Zeitsch. physikal. Chem.*, 1894, **13**, 539; 1896, **20**, 19) and of the author (Trans., 1901, **79**, 238), concordant values are obtained for the constant corresponding with the dissociation equilibrium, $KI_3 \rightleftarrows KI + I_2$, without taking into account the "salting out" effect exerted by the electrolytes present in the aqueous solution on the iodine distribution. In so far as iodide and tri-iodide are concerned, the magnitude of this effect is therefore in all probability very small, but the mercuric iodide present in the solutions examined introduces another factor, the influence of which must be considered more closely.

It is probable that the effect of the presence of the complex mercuric iodide will be to displace iodine from the aqueous solution, and although it is not possible to estimate its magnitude, it is quite certain that the extent of the displacement will increase with increasing concentration of the mercuric iodide. In consequence of this action, the calculated values of m/n recorded in the foregoing tables are slightly greater than the true values, although it can be shown that the differences involved must be very small, even in the case of the most concentrated mercuric iodide solutions.

In a paper on the influence of strong electrolytes in distribution phenomena (*Zeitsch. physikal. Chem.*, 1906, **56**, 605), the author has calculated the relative changes produced by equivalent quantities of various electrolytes on the distribution of iodine between water and carbon disulphide. The numbers vary from about 10 to 30 per cent.

If now we assume that the alteration in the distribution of the iodine in the experiments recorded in this paper corresponds with a displacement of 20 per cent. per mol. of mercuric iodide, then for the most concentrated solution examined (see expt. 13), the distribution ratio CS_2/H_2O increases from 620 to 629, and the value of m/n becomes 1·81 instead of 1·80. From this it is evident that the influence of the "salting out" action on the calculated values of m/n is almost negligibly small.

The second approximation is involved in the fact that no account has been taken of the changes in volume which occur when mercuric iodide is dissolved in the potassium iodide solutions. In the case of the 0·1 and 0·2 molar potassium iodide solutions, the maximum volume changes involved were ascertained by accurate density measurements. On dissolving 0·0406 mol. of mercuric iodide in a litre of 0·1 molar potassium iodide solution, the increase in volume was found to be 0·31 per cent., whilst the increase on dissolving 0·0720 mol. of mercuric iodide in a litre of 0·2 molar potassium iodide solution amounted to 0·53 per cent. The true values of the concentrations of the potassium and mercuric iodides in the case of the solutions examined in expts. 7 and 13 are therefore less than the values actually used in the calculations by these amounts respectively. It is found, however, that the values of m/n are practically unaltered when these small volume changes are taken into account.

From the above considerations relating to the influence of the "salting out" effect, and of the volume changes which take place in the solution of mercuric iodide, it appears justifiable to conclude that the values of m/n recorded in the tables approximate very closely to the true values.

An inspection of the figures in the last column of tables I and II shows that m/n is not constant, but for a given potassium iodide solution it decreases regularly with increasing concentration of the mercuric iodide. The variation is most strongly marked in the case of the more dilute solutions of the alkali iodide. Similar results are obtained whether carbon disulphide or carbon tetrachloride is used for the indirect estimation of the free potassium iodide in the aqueous solution.

The variation of m/n is an indication that the solutions contain, in general, more than one complex potassium mercuric iodide. Corresponding with $m/n = 2$, which appears to be the higher limiting value of the ratio, the chief complex electrolyte in solutions which contain relatively little mercuric iodide has the composition $2KI,HgI_2$. As the relative proportion of mercuric iodide in the solution increases, this complex electrolyte is gradually transformed, a second complex electrolyte containing a relatively larger proportion of mercuric iodide being formed in gradually increasing quantities.

It will be observed that all the values of m/n are confined between the limits 1·5 and 2, and if the second complex iodide has the composition $3KI,2HgI_2$, the first must be almost completely transformed into this in the case of solutions for which the experimentally determined ratio m/n is not much greater than 1·5. On the other hand, if the second complex iodide corresponds with the formula KI,HgI_2, such solutions must contain approximately equimolar quantities of the two complex iodides $2KI,HgI_2$ and KI,HgI_2.

Sherrill's measurements (*loc. cit.*) of the changes which take place in the freezing points of potassium iodide solution when these are saturated with mercuric iodide may be utilised for the purpose of differentiating between these two possibilities. Corresponding with the equations:

$$(1)\quad 2HgI_2 + 3KI = 2HgI_2,3KI,$$

$$(2)\quad 2HgI_2 + 3KI = HgI_2,2KI + HgI_2,KI,$$

the addition of 2 mols. of mercuric iodide should reduce the total number of molecules present in the solution by two according to (1) and by one according to (2). The data for 0·736, 0·511, and 0·237 molar potassium iodide solutions correspond with reductions in the total number of molecules of 1·64, 1·90, and 1·96 respectively. These results therefore lend support to the view that the complex iodide $3KI,2HgI_2$ is the chief constituent of solutions which contain relatively large proportions of mercuric iodide.

The experimental results obtained by the method of inquiry described in this paper are in agreement with those obtained by other methods. According to solubility measurements (*loc. cit.*) the molar ratio KI/HgI_2 for solutions saturated with mercuric iodide falls from 2·20 for a 0·031 to 1·82 for a 1·0 molar potassium iodide solution. The smaller value of the ratio is an indication that a complex iodide containing relatively more mercury than $2KI,HgI_2$ is present in the more concentrated solutions. The electromotive force measurements of Sherrill (*loc. cit.*) indicate that the complex iodide $2KI,HgI_2$ is the chief component of solutions which contain relatively little mercuric iodide, whilst the dynamic measurements of Walton (*loc. cit.*) support this view, and show, further, that the molar ratio of potassium iodide in combination with mercuric iodide diminishes with increasing concentration of the latter, and approximates to the limiting value 1·5 in the case of the saturated solutions.

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XCVII.—*Solubility of Lead Sulphate in Concentrated Solutions of Sodium and Potassium Acetates.*

By John Jacob Fox.

The investigation described in this paper was undertaken mainly with the object of ascertaining what changes, if any, take place in solid lead sulphate when brought into contact with aqueous solutions of sodium and potassium acetates; and, further, to what extent the solubility of the sulphate is influenced by increasing the concentration of the acetate.

Lead sulphate differs from the insoluble sulphates of barium, strontium, and calcium in the ease with which it may be dissolved in a variety of salt solutions. Of the three sulphates mentioned, calcium sulphate is the only one which can be dissolved by acetates to any degree comparable with that of lead sulphate, and it is also fairly readily soluble in ammonium sulphate; but as it is considerably more soluble in water than either barium, strontium, or lead sulphate, its increased solubility might be anticipated if we suppose that calcium acetate is formed, and that more sulphate is dissolved to restore the equilibrium of the solution. Such an explanation might, however, be equally applicable to barium and strontium sulphates, but breaks down, since these two are insoluble in aqueous ammonium acetate solutions.

A more probable explanation is the formation of complex ions (such as $Ca(NH_4)_n$), due to double salt formation. It has been shown that calcium sulphate dissolves in ammonium sulphate solution, and deposits crystals corresponding in composition with $Ca(NH_4)_2(SO_4)_2,2H_2O$ (Bell and Faber, *J. Physical Chem.*, 1907, **2**, 492). A similar observation has been made by the author in the case of the solubility of lead sulphate in ammonium acetate (Proc., 1907, **23**, 200). It was there shown that when the concentration of the ammonium acetate was about $3N$, crystals of ammonium lead sulphate, $Pb(NH_4)_2(SO_4)_2$, were deposited by the solution, the increase of solubility of the lead sulphate at the same time being most marked for stronger ammonium acetate. Now it is obvious that if some of the sulphate is deposited from the solution in the form of ammonium lead sulphate, whilst at the same time the solubility of the lead increases considerably, the equilibrium system cannot be one solely of the solubility of lead sulphate. In reality, it is an equilibrium system for the solubility of lead acetate or possibly ammonium lead acetate in the peculiar circumstances of having a solid phase or phases consisting of sulphates. The matter is still further complicated by the fact that lead sulphate is fairly soluble in ammonium sulphate. Since neither sodium nor potassium sulphate dissolves lead sulphate, it seemed possible that simpler systems would result from the investigation of the solubility in sodium and potassium acetates.

The only measurements of such solubilities made hitherto are those of Dibbits (*Zeitsch. anal. Chem.*, 1874, **13**, 139), and one experiment recorded by Noyes (*Amer. Chem. J.*, 1905, **27**, 747), who worked with solutions up to $0·4$-N concentration. The formulæ deduced by Noyes from these dilute solutions do not apply to concentrated solutions.

The systematic determination of the solubility of lead sulphate in potassium and sodium acetates described below shows that the solubility increases regularly with increasing concentration of the acetates, but the increase of solubility is much greater than the corresponding increase in the concentration of the acetate. In other words, the solubility of the lead sulphate is not a linear function of the alkali acetate, and the nature of the curve suggests that the solubility of the lead is some function of the alkali acetate, involving powers higher than unity. Expressing the reaction by the equation:

$$PbSO_4 + 2RC_2H_3O_2 = R_2SO_4 + Pb(C_2H_3O_2)_2,$$

would give, as the simplest expression:

$$C_{PbSO_4} \times C^2_{Acetate} = k.C_{Sulphate} \times C_{Pb(C_2H_3O_2)_2}.$$

This expression would be modified by the decreased solubility of the alkali sulphate in the alkali acetate, evidence of which was obtained from the examination of the systems alkali acetate–alkali sulphate. However this might affect the main equation, the solubility expression would still include the square of the concentration of the alkali acetate, provided that the equation actually represents the reaction during dissolution. This matter was solved from the examination of the equilibria solutions for lead sulphate–potassium acetate. None of these solutions contained any sulphate, although the quantity of lead dissolved was fairly considerable, amounting in some cases to more than 19 per cent., calculated as lead acetate. It follows, therefore, that these solutions contained lead and potassium acetates only, and that the solubility of lead sulphate in potassium acetate is due exclusively to the formation of lead acetate and potassium sulphate.

The solid phase consists of lead potassium sulphate, which is practically insoluble as such in the acetate, careful tests showing that no lead acetate was present in the solid phase. The formation of the salt $PbK_2(SO_4)_2$ on mixing solutions of lead acetate and potassium sulphate may be accounted for by the preliminary formation of complex acetates, such as $PbK_2(C_2H_3O_2)_4$. This would then react with more potassium sulphate to give insoluble $PbK_2(SO_4)_2$. It is difficult otherwise to account for the uniform composition of the precipitate, even when an excess of potassium sulphate solution is used.*

The absence of sulphates in the equilibria solutions in the case of potassium acetate confirms Noyes's supposition that the solubility of lead sulphate is due to the formation of non-ionised lead acetate by metathesis, and it may not unreasonably be assumed that a similar explanation holds for both ammonium and sodium acetates.

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* Holmes and Sageman (Trans., 1907, **91**, 1611) conclude that potassium sulphate exists in solution as $(K_2SO_4)_2$. The formation of lead potassium sulphate would, on this view, take place thus:

$$Pb(C_2H_3O_2)_2 + (K_2SO_4)_2 = PbK_2(SO_4)_2 + 2C_2H_3O_2K.$$

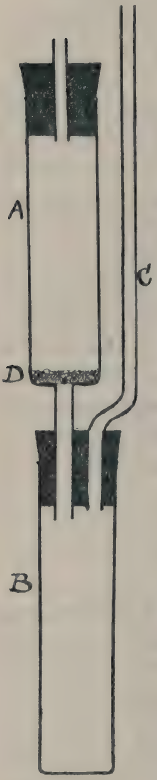
In the case of ammonium acetate, the formation of ammonium lead sulphate with the greater concentrations of acetate bears this out, but sodium acetate did not give rise to any double salt of this kind. In all the cases examined, the solid phases for the sodium acetate solutions consisted of lead sulphate. When the saturated solutions were separated from the solid and cooled, crystals of sodium sulphate decahydrate separated from the strongest solutions, pointing to the existence in the solution of lead acetate and sodium sulphate. The absence of the double salt in the solid phases in the sodium systems is especially interesting in view of the fact that the curve for the solubility of sodium sulphate in sodium acetate solutions is of an entirely different character from that of potassium sulphate in potassium acetate solutions. The amount of potassium sulphate which can be dissolved in potassium acetate solutions of increasing concentration reaches a point, in the stronger solutions, where it is far less than the equivalent quantity of lead dissolved in the acetates. But with sodium acetate the smallest amount of sodium sulphate found was 14·4 mols. per 1000 mols. of water; and this quantity is greater than any of the quantities of lead which could be dissolved in the acetate solutions. Consequently the sodium acetate–lead sulphate equilibrium solutions are never saturated as regards sodium sulphate, which therefore does not appear in the solid phases either alone or as double salt with lead sulphate.

EXPERIMENTAL.

The solubility determinations were carried out at a temperature of 25° ± 0·1°. In some cases dissolution was effected by shaking the lead sulphate in a well-stoppered bottle half filled with the cold solution, and completely immersed in the thermostat. In other cases, saturation was obtained by heating the solution in presence of excess of the solid at a higher temperature and placing the vessel in the thermostat at 25°, the solution being well shaken from time to time and then allowed to settle. The apparatus shown in Fig. 1 was used to obtain saturated solutions without stirring or shaking.

A tube about four inches in length and one inch in diameter, *A*, was drawn out as shown, and fitted by a rubber stopper into tube *B*, an air vent, *C*, being provided. The tube *A* was plugged with asbestos at *D*, and the solid was placed on the asbestos. The solvent was poured into *A*, and allowed to percolate slowly into *B*, which also contained some solid. After all the liquid had passed into *B*, it was transferred to *A* again. The whole apparatus was immersed in the thermostat as far as the stopper of *A*. The percolation was continued until the density of the solution became constant, the density being determined in a Meyerhoffer pipette (*Zeitsch. physikal. Chem.*, 1899, **28**, 466). In many cases, saturation was complete in a few hours, especially when the solid phase suffered no change. When, however, the solid altered, considerably longer periods were required, and in a few cases, more especially with the more concentrated solutions, two or three days were found to be necessary before the density of the solution became constant.

FIG. 1.



A point of some importance arose in connexion with the distilled water used. In one case ordinary distilled water, which had been boiled to expel dissolved gases, gave a solution of which the density was 1·16421. A similar experiment was carried out, except that the distilled water was prepared in a platinum still and condenser and collected in a well steamed-out Jena flask. The density of the resulting solution in this case was 1·16431. The difference is very small. In all the subsequent experiments distilled water, which had been previously boiled, was used. Although water of this kind is unsuitable for very dilute solutions, it is apparently sufficiently satisfactory for concentrated solutions.

The lead sulphate was prepared by treatment of a solution of lead acetate with sulphuric acid, the precipitate being washed with diluted sulphuric acid and finally with a little water; it was then dried, gently ignited, and powdered. Prepared in this way, one gram of the solid gave no alteration in weight on evaporation to dryness with sulphuric acid and gentle ignition.

For convenience of reference the solubilities in potassium and sodium acetates are treated separately.

Solubility of Lead Sulphate in Potassium Acetate Solutions at 25°.

The potassium acetate was prepared by treatment of potassium hydrogen carbonate with slightly diluted glacial acetic acid, in the proper proportion. The solution so obtained was evaporated to small bulk to expel carbon dioxide and diluted as required. It was usually found to be slightly acid to phenolphthalein, and the requisite quantity of potassium hydroxide solution (freed from impurities by alcohol) was added to yield a neutral solution. A less troublesome method was the use of pure potassium acetate, tested before use as to its neutrality to phenolphthalein and for impurities.

About 25 c.c. of potassium acetate solution were agitated for several days with excess of lead sulphate, the prolonged agitation being essential, since the preliminary dissolution of the lead sulphate which must take place is slow on account of the difficulty in dissolving sulphate in potassium acetate. When the saturation point is approached from a higher temperature, the liquid with the solid must be thoroughly agitated in the thermostat. Lead potassium sulphate is so little soluble in potassium lead acetate solutions that prolonged shaking is necessary to ensure equilibrium.

The composition of the solutions was ascertained by determining the proportions of lead and potassium, the precipitated sulphate being boiled for some time with diluted sulphuric acid in order to decompose any potassium lead sulphate which might be formed. A portion of the solutions was acidified with hydrochloric acid, raised to the boiling point to dissolve lead chloride, and treated with barium chloride solution. As no precipitate of barium sulphate formed even after long boiling, it was thought possible that complex acetosulphates might be formed, or that the inability to form sulphions might prevent the precipitation of barium sulphate, similar to the prevention of the precipitation of silver chloride from mercury solutions, described by Hewitt (Proc., 1907, **23**, 10).

A test was therefore made with lead sulphate and potassium acetate solution in large excess to ascertain whether the sulphate could be estimated under these conditions. 0·4272 Gram of lead sulphate was treated with 50 c.c. of potassium acetate solution; hydrochloric acid was added, and the whole was boiled until a clear solution resulted. The conditions are then similar to those

Composition of Saturated Solutions of System $KC_2H_3O_2 - Pb(C_2H_3O_2)_2$ *in Solution; Solid Phases,* $PbSO_4$ *and* $PbK_2(SO_4)_2$, *at* 25°.

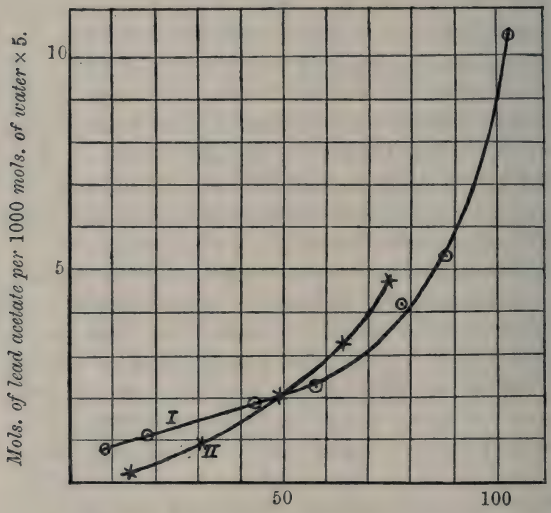
	Percentage.			Molecules per 1000 molecules H_2O.	
	Potassium acetate.	Lead acetate.	Water.	Potassium acetate.	Lead acetate.
1	4·33	2·54	93·13	8·53	1·51
2	9·03	3·55	87·42	18·95	2·25
3	17·81	5·43	76·76	42·57	3·92
4	22·07	5·95	71·98	56·27	4·58
5	26·58	9·83	63·59	76·69	8·57
6	28·82	11·40	59·78	88·45	10·57
7	28·93	19·41	51·66	102·80	20·82

which occur on attempting to estimate the sulphate, if present, in the actual solubility experiments. Barium chloride produced an immediate precipitate, which gave 0·3165 $BaSO_4$, equivalent to 0·4286 $PbSO_4$.

The results are plotted in Fig. 2, curve I, the curve being regular. The abscissæ are molecules of potassium acetate, and the scale of the ordinates is five times that of the abscissæ, the enlarged scale of the ordinates exaggerating the errors in the determinations.

The solid phases consisted of sulphates only, and were anhydrous, containing traces of adherent moisture only. The following are the results for the solids in two cases:

FIG. 2.



Mols. of alkali acetate per 1000 *mols. of water.*
I. *Solubility of lead sulphate in potassium acetate.*
II. ,, ,, *sodium acetate.*

0·9792 gave 0·6348 $PbSO_4$ = 64·83.
0·8668 ,, 0·6512 $PbSO_4$ = 75·13 per cent.

In neither case was there any alteration of weight on evaporation with sulphuric acid.

The double salt, potassium lead sulphate, was prepared by mixing a solution of lead acetate with a solution of potassium sulphate, having the lead acetate in excess. The solutions were well shaken for some time, and the solid collected, washed two or three times with a solution of potassium acetate, and finally with a little alcohol. The air-dried product, which is amorphous, gave on analysis the following results:

0·6482 gave 0·4108 $PbSO_4$ and 0·2370 K_2SO_4.

$PbSO_4 = 63·38$; $K_2SO_4 = 36·36$.

$PbK_2(SO_4)_2$ requires $PbSO_4 = 63·48$; $K_2SO_4 = 36·52$ per cent.

The same compound is formed when the amount of lead sulphate shaken with potassium acetate solution is not present in excess.

System: Potassium Acetate (Solution)–Potassium Sulphate at 25°.

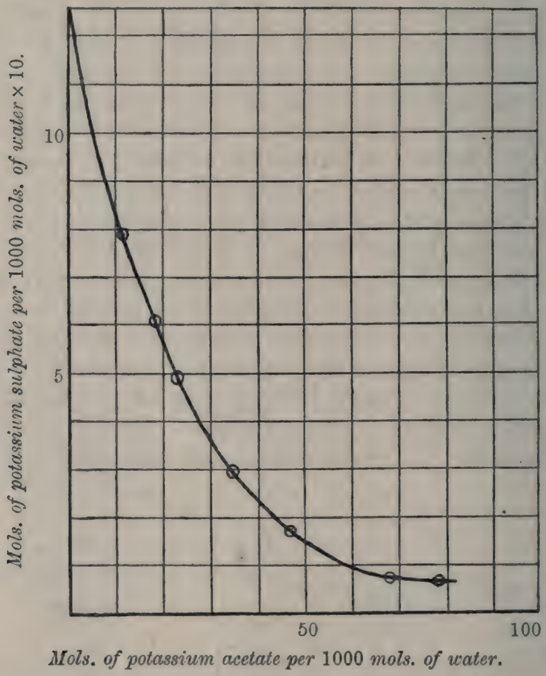
This system was investigated to ascertain the influence on the solubility of potassium sulphate of the increased concentration of the potassium acetate, for since potassium sulphate can be formed from the lead sulphate by metathesis, it seemed desirable to determine the extent to which it could remain dissolved. On mixing a saturated aqueous solution of potassium sulphate with a concentrated solution of potassium acetate, an immediate precipitate of potassium sulphate formed, so that obviously potassium sulphate is less soluble in potassium acetate solution than in water. The solutions for investigating this system were obtained by shaking with excess of solid potassium sulphate or by heating potassium acetate solution with potassium sulphate in a water-bath and allowing to cool in the thermostat, shaking frequently. The analysis of the saturated solutions presented no difficulty; but it was necessary to boil the precipitated barium sulphate for several hours to remove all the potassium chloride, barium sulphate having a tendency to retain sodium and potassium unless this is done.

Composition of the Solutions.

	Percentage.			Molecules of salt per 1000 molecules H_2O.	
	Potassium acetate.	Potassium sulphate.	Water.	Potassium acetate.	Potassium sulphate.
1	6·11	6·65	87·24	12·85	7·87
2	8·68	5·09	86·23	18·47	6·10
3	11·29	3·99	84·72	24·45	4·86
4	15·59	2·35	82·06	34·78	2·96
5	20·12	1·23	78·65	46·90	1·62
6	29·95	0·39	69·66	79·00	0·58

These results give a regular curve (Fig. 3), the scale for potassium sulphate being five times that of potassium acetate. The solubility of potassium sulphate in water is 10·75 per cent. (Seidell, *Solubilities of Inorganic and Organic Substances*), which is equivalent to 12·47 molecules of potassium sulphate per 1000 molecules of water. If the curve is produced it will be found to pass almost through the point on the ordinate corresponding with the solubility of potassium sulphate in water. The striking feature of this system is the rapid decrease in the solubility of potassium sulphate with increasing concentration of the acetate. To a certain extent the absence of sulphate in the liquid of the systems $[KC_2H_3O_2 + Pb(C_2H_3O_2)_2] - [PbSO_4 + PbK_2(SO_4)_2]$ is no doubt connected with the marked decrease of solubility of the sulphate in the potassium acetate. The solid phase in the system potassium acetate–potassium sulphate was found to consist of potassium sulphate containing a little adhering solvent.

FIG. 3.



It has already been shown that the solubility of lead sulphate in potassium acetate is due to the formation of lead acetate, the solubility being influenced in all probability by the solid sulphate phases. Whether the sulphates exerted any influence could be ascertained by determining the solubility of lead acetate in potassium acetate solutions. One or two such saturated solutions were obtained by using lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$, with potassium acetate solutions. The solubility in water alone was determined, and found to be 35·9 per cent. of lead acetate (anhydrous).

Composition of the Solutions.

	Percentage.			Molecules per 1000 molecules H_2O.	
	Potassium acetate.	Lead acetate.	Water.	Potassium acetate.	Lead acetate.
1	13·87	38·05	48·06	52·97	43·90
2	15·40	36·91	47·69	59·25	42·88
3	0	35·90	64·10	0	31·03

A crystalline solid separated from the solutions on cooling, and was found to correspond with $Pb(C_2H_3O_2)_2,3H_2O$. The solubility of lead acetate in potassium acetate is seen to be greater than in water. These solubilities are not very different as percentages, but, expressed on the basis of a fixed quantity of water, the difference becomes marked.

If lead acetate in solutions gave rise to ions, the addition of potassium acetate, which is partly electrolytically dissociated, should result in a lowering of the solubility of lead acetate. Since, however, the solubility increases, the conclusion that lead acetate gives no ions receives additional support.

The ratio $C_2H_3O_2K/Pb(C_2H_3O_2)_2$ in this system is less than in the system potassium acetate–lead sulphate, the concentration of the lead being much less in the latter system. The difference must be ascribed to the presence of the sulphate solid phases, the tendency of which would be to lower the solubility of the lead.

Solubility of Lead Sulphate in Sodium Acetate Solutions at 25°.

The sodium acetate solutions were prepared from sodium hydrogen carbonate and acetic acid, as in the case of potassium acetate, or by using recrystallised sodium acetate. The analyses were conducted as in the previous cases, but as the solutions contained sulphate it was necessary to determine this constituent. In all the cases examined, the proportion of sulphate in solution corresponded with the amount of lead present, but was calculated to sodium sulphate, since sodium sulphate decahydrate crystallised from the solutions on cooling.

Composition of the Solutions.

	Percentage.				Molecules per 1000 molecules H_2O.		
	Sodium acetate.	Lead acetate.	Sodium sulphate.	Water.	Sodium acetate.	Lead acetate.	Sodium sulphate.
1	6·69	0·78	0·34 (0·38)	92·19	15·92	0·47	0·47
2	11·76	2·73	1·26 (1·26)	84·25	30·62	1·80	1·80
3	16·90	5·70	2·49 (2·58)	74·91	49·49	4·22	4·22
4	19·92	8·24	3·60 (3·70)	68·24	64·03	6·69	6·69
5	21·51	10·75	4·68 (4·77)	63·10	74·78	9·41	9·41
6	6·95	0·81	0·35 —	91·90	—	—	—

The figures in brackets are calculated from the barium sulphate obtained. The form of the curve (Fig. 2, curve II) somewhat resembles the curve for the solubility of lead sulphate in potassium acetate, the scale of ordinates being five times that of the abscissæ.

The fact that the amount of sulphate in solution is equivalent to the amount of lead necessitates that the solid phase should remain as lead sulphate, and this was found to be the case, the separated solid containing very small amounts of sodium salts and acetates due to the adhering solvent. No double salt of lead and sodium was obtained.

System: Sodium Acetate (Solution)–Sodium Sulphate Decahydrate at 25°.

This system was investigated similarly to the corresponding potassium salts, but some difficulty was experienced in obtaining representative portions of the liquid at 25°, owing to the tendency of the sodium sulphate to crystallise when the solution cooled slightly. The temperature-coefficient for the solubility of sodium sulphate in water in the neighbourhood of 25° is large (about 1·3 per cent.), and this renders it rather difficult to work with clear solutions.

Composition of the Solutions.

	Percentage.			Molecules per 1000 molecules H_2O.	
	Sodium acetate.	Sodium sulphate.	Water.	Sodium acetate.	Sodium sulphate.
1	0	21·9	78·1	0	35·5
2	4·10	17·72	78·18	11·5	28·7
3	7·71	16·48	75·81	22·3	27·5
4	12·58	13·50	73·92	37·4	23·1
5	16·26	11·50	72·24	49·4	20·2
6	20·63	8·10	71·27	63·5	14·4

The solubility of sodium sulphate decahydrate in water is taken from Seidell's *Solubilities of Inorganic and Organic Compounds.* It will be seen that the curve, ordinates and abscissæ being drawn to the same scale (Fig. 4), is nearly a straight line. In this respect the solubility of sodium sulphate is entirely different from that of potassium sulphate in potassium acetate, and largely explains the inability of sodium sulphate to form a double sulphate with lead.

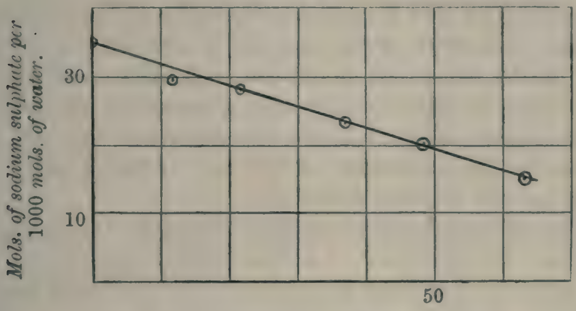
The solid phase in the system sodium acetate–sodium sulphate decahydrate consisted wholly of sodium sulphate decahydrate, which formed in large crystals on cooling.

One saturated solution of lead acetate in sodium acetate was prepared, with the following results:

12·58 per cent. of sodium acetate, 32·40 per cent. of lead acetate, and 55·02 per cent. of water; corresponding with 50·2 molecules of sodium acetate and 32·6 molecules of lead acetate per 1000 molecules of water.

The ratio sodium acetate/lead acetate is of the same order of magnitude as the ratio potassium acetate/lead acetate found before, and although one solubility only is here determined, it points to the conclusion that the reason for the solubilities of lead sulphate in the two acetates is the same despite the differences in the solid phases, namely, the formation of lead acetate in solution.

FIG. 4.



Mols. of sodium acetate per 1000 *mols. of water.*

EAST LONDON COLLEGE.

XCVIII.—*The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part II. Brilliant-green and Malachite-green.*

By NEVIL VINCENT SIDGWICK and TOM SIDNEY MOORE.

IN a previous paper (*Zeitsch. physikal. Chem.*, 1907, **57**, 385) we have discussed the rate of change of brilliant-green (the salt of tetraethyldiaminotriphenylcarbinol) in the presence of hydrochloric acid and of alkali. In order to determine the influence on these velocities of the acid used and of the dye, we have examined the rate of reaction of brilliant-green with nitric acid, and also that of malachite-green, the corresponding tetramethyl compound, with nitric and hydrochloric acids and with alkali.

The method of investigation was the same as in our previous work, the depth of colour of the solution being measured in a Donnan tintometer against a standard solution of the same dye. The temperature was in all cases 21·2°.

In our previous paper we have stated that two observers may obtain readings of the same colour which differ considerably from one another, and yet stand in a constant ratio. Further experience has shown that, whilst this is undoubtedly the case, the discrepancy is due to some difference in the manner of observing the colour, and probably in the focussing of the eye, for with practice it may be made to disappear. As the value of the constants obtained depends only on the relative concentrations, this difference does not affect it; but it is an obvious convenience if the two observers adopt the same method and secure identical readings.

In many of the velocity experiments which follow, the readings were taken by the two of us alternately, giving two different series of values for the same experiment. In such cases the series are distinguished by the letters *a* and *b* (for example, expt. 24*a*, 24*b*).

I. *Brilliant-green and Nitric Acid.*

We are indebted to Mr. Manley for giving us some specially purified nitric acid which he and Dr. Veley had used for determining the conductivity. At his suggestion it was treated for some time with a stream of ozonised oxygen to destroy any traces of nitrous acid, the ozone being then removed by a stream of dry air. After this treatment it gave no test for nitrous acid. A 0·0212*N*-solution of this was made up, and was kept in a bottle wrapped in paper to exclude the light. It remained for more than a year without showing any signs of the formation of nitrous acid.

The brilliant-green was employed as before in the form of the oxalate $[C_6H_5\cdot C(C_6H_4\cdot NEt_2)_2\cdot OH,H_2C_2O_4]$, and was purified by recrystallisation. A *N*/1000-solution of this was made up (containing 0·492 gram per litre), and from this a *N*/20,000-solution was prepared of which 10 c.c. were used in each experiment. This volume was diluted with water in the tube of the tintometer, its colour measured, and then the necessary amount of acid added and the whole made up to 50 c.c. Thus the initial concentration of the dye was *N*/100,000.

A. *Action of Nitric Acid on the Dye-salt.*

If the solution of the dye-salt is acidified, its colour gradually diminishes, owing to the formation of the (comparatively) colourless acid salt, equilibrium being attained after the lapse of several hours. If A be the length of the balancing column before the addition of acid, and x the length after equilibrium is reached, it follows that the solution now contains a concentration of the dye-salt, x, whilst the difference $A-x$ represents the amount of acid salt produced. It was found (as with hydrochloric acid) that if s be the number of c.c. of acid added, the expression $\frac{x \, . \, s}{A-x}$ is constant: that is to say,

$$C_{\text{dye-salt}} \times C_{\text{acid}} = r \times C_{\text{acid salt}}.$$

This result is to be expected if the reaction has the form

$$\text{Dye-salt} + \text{H}^{\cdot} = \text{Acid salt},$$

for if k_1 is the velocity constant for the reaction from left to right, and k_2 that of the reverse reaction, we have at equilibrium:

$$k_1sx = k_2(A-x) \quad \text{or} \quad \frac{x \, . \, s}{A-x} = \frac{k_2}{k_1} = r.$$

The values of k_1 and k_2 may be obtained by observing the fall of colour at definite intervals of time. By integrating the expression for the diminution of colour

$$-\frac{dx}{dt} = k_1sx - k_2(A-x),$$

since $\frac{k_2}{k_1} = r$, and $x = A$ when $t = 0$,

we obtain $\log\frac{sA}{s+r} - \log\left(x - \frac{rA}{s+r}\right) = (k_2+k_1s)t.$

The value of r was taken as 11·40, the mean of nine results, of which the extreme limits were 11·13 and 11·58, being 11·38.

The following is a summary of the results obtained in the velocity experiments. The fifth column gives the maximum departure of any observed value of k_2+k_1s from the mean.

It will be seen that (as was the case with hydrochloric acid) they rise as the amount of acid falls, and the expression $k_2s^{\frac{1}{3}}$ is constant.

Summary: Brilliant-green and Nitric Acid.

Expt.	Acid in c.c. $=s$.	No. of readings.	k_2+k_1s, mean (decimal).	Diff.	k_2 (natural).	k_1 (natural).	$k_2s^{\frac{1}{3}}$.
1 *a.*	16·10	10	0·0160	0·0004	0·0153	0·00134	0·0385
b.	16·10	11	0·0162	0·0007	0·0155	0·00136	0·0390
2 *a.*	12·11	14	0·0153	0·0007	0·0171	0·00150	0·0392
b.	12·11	15	0·0153	0·0007	0·0171	0·00150	0·0392
3 *a.*	10·04	9	0·0145	0·0008	0·0178	0·00156	0·0383
b.	10·04	10	0·0148	0·0006	0·0181	0·00159	0·0391
4 *a.*	9·00	11	0·0141	0·0010	0·0182	0·00159	0·0378
b.	9·00	15	0·0140	0·0007	0·0180	0·00158	0·0374
5 *a.*	7·96	10	0·0141	0·0007	0·0191	0·00168	0·0382
b.	7·96	11	0·0144	0·0008	0·0195	0·00171	0·0390
6 *a.*	6·00	7	0·0139	0·0008	0·0210	0·00184	0·0381
b.	6·00	6	0·0141	0·0011	0·0213	0·00187	0·0387
7 *a.*	4·17	13	0·0138	0·0008	0·0233	0·00204	0·0375
b.	4·17	13	0·0140	0·0010	0·0236	0·00207	0·0379
						Mean =	0·0384

B. *Action of Nitric Acid on the Carbinol of Brilliant-green.*

If a dilute solution of brilliant-green is treated with alkali, the colour disappears and a solution of the carbinol,

$$C_6H_5{\cdot}C(C_6H_4{\cdot}NEt_2)_2{\cdot}OH,$$

is formed. On adding excess of acid to this, three reactions take place: (1) the formation of dye-salt; (2) that of the acid salt; (3) the dissociation of the latter into the dye-salt and acid. The initial concentration A of the carbinol is known, and that of the dye-salt at any time t is given by the value of x.

If y is the concentration of the acid salt at this time, then that of the carbinol is $A-x-y$. If the formation of the dye-salt from the carbinol is assumed to be unimolecular, and its velocity constant is M (which is presumably a function of the acid present, but remains constant in each experiment), then the rate of formation of dye-salt in reaction (1) is $M(A-x-y)$, whilst its rate of disappearance $\frac{dy}{dt}$ in reactions (2) and (3) we can calculate from the last series of measurements; thus the complete differential equation is

$$\frac{dx}{dt} = M(A-x-y) - \frac{dy}{dt},$$

where

$$\frac{dy}{dt} = k_1sx - k_2y.$$

On integrating this under the condition that when $t=0$, $x+y=0$, we obtain, as was shown before,

$$x = \frac{Ak_2}{k_2+k_1s} - A\frac{k_2-M}{k_2+k_1s-M}e^{-Mt},$$
$$- A\frac{k_1sM}{(k_2+k_1s)(k_2+k_1s-M)}e^{-(k_2+k_1s)t} \quad . \quad . \quad . \quad (1)$$

The solution of this equation by the method of trial, as adopted in our previous work, is extremely laborious. The calculation is very much simplified by the use of a graphical method,[*] which we owe to

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[*] If we substitute

$$\frac{1}{y} = t(k_2-M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$P = e^{k2t}\left(\frac{k_2}{k_2+k_1s} - \frac{x}{A}\right) + \frac{k_1s}{k_2+k_1s}c^{-k1st}$$

and

$$\frac{P}{Q} = k_1st(c^{-k_1st} - P)$$

in the above equation, we get

$$\frac{1}{c^y} = P - y\frac{P}{Q}.$$

Mr. H. G. J. Moseley, of Trinity College, to whom our best thanks are due.

The carbinol solution was prepared as before by adding a slight excess of sodium hydroxide to the dye-salt, a correction in the value of s for this excess being made. The solution was $N/50,000$, and in each experiment 25 c.c. were taken and made up to 50 c.c., the solution in the tube being thus $N/100,000$. The carbinol solution was always prepared on the day on which it was used.

The values of k_2 and k_1s are calculated from the equation $k_2s^{\frac{1}{3}} = 0{\cdot}0384$.

The results obtained are summarised in the following table.

Brilliant-green Carbinol and Nitric Acid.

Expt.	Acid in c.c. $= s$.	No. of readings.	M.	Diff.	$Ms^{\frac{2}{3}}$.
8 *a.*	11·98	18	0·0150	0·0012	0·0785
b.	11·98	18	0·0150	0·0010	0·0785
9 *a.*	9·96	13	0·0181	0·0011	0·0838
b.	9·96	14	0·0182	0·0011	0·0842
10 *a.*	7·96	16	0·0205	0·0015	0·0817
b.	7·96	15	0·0206	0·0016	0·0821
11 *a.*	5·89	13	0·0265	0·0020	0·0864
b.	5·89	12	0·0254	0·0025	0·0829
				Mean =	0·0823

As in the case of hydrochloric acid, the velocity constant is inversely proportional to the square of the cube root of the concentration of the acid.

II. *Malachite-green.*

A corresponding series of experiments was carried out to determine the value of these velocity constants for the homologous malachite-green, the salt of tetramethyldiaminotriphenylcarbinol. The substance was purified in the same way as the ethyl compound, and the method

The values of y which satisfy this equation are given as the co-ordinates of the points of intersection of the curve

$$z = e^{\frac{1}{y}} \qquad (3)$$

with the line

$$z = P - y\frac{P}{Q} \qquad (4)$$

The curve (3) may be drawn once for all. To each observation of t and x correspond particular values of P and Q, which are to be calculated from the above equation; and using these values, the line corresponding to the observation is drawn. In general, the line cuts the curve in two points, one of which gives a spurious root corresponding to $k_2 + k_1s = M$, the other giving the proper root for the observation in question. The value of M is then found by substitution in equation (2).

of working was identical. The oxalate has the composition expressed by the formula $2C_{23}H_{24}N_2,3C_2H_2O_4$, and the stock solution, $N/1000$ with respect to the cation of the dye, contained 0·463 gram per litre.

A. *Malachite-green and Alkali.*

The alkali used was 0·0158N-sodium hydroxide, and the temperature, as in all cases, was 21·2°. The velocity constants are calculated on the unimolecular formula $K=\frac{1}{t}\log\frac{A}{x}$, using decimal logarithms.

In this case the calculation can be begun at any point, the value of x when $t=0$ being used as A; and hence the earliest stage of the reaction, which shows the usual irregularities, can be excluded. In expts. 12—18, 10 c.c. of $N/20,000$-dye solution were used, and the initial value of the colour was about 10 cm. In expt. 19, to enable a sufficient number of readings to be taken in spite of the great velocity of the change, 15 c.c. of dye were used, and the initial colour was therefore about 15 cm.

Summary : n = c.c. alkali added.

Expt.	n.	No. of readings.	K.	Diff.	K/n.
12	0·82	20	0·0102	0·0007	0·0124
13	1·22	10	0·0146	0·0005	0·0120
14	1·47	19	0·0179	0·0007	0·0122
15	1·70	12	0·0206	0·0007	0·0121
16	1·95	14	0·0227	0·0008	0·0116
17	2·49	7	0·0297	0·0013	0·0119
18	2·54	6	0·0295	0·0006	0·0116
19	3·10	15	0·0362	0·0010	0·0117
				Mean =	0·0121

It is evident, therefore, that, as with brilliant-green, the reaction is unimolecular, and the constant approximately proportional to the amount of alkali present; or, in other words, the rate of formation of the carbinol is proportional to the product of the concentrations of the cation of the dye and hydroxyl.

B. *Malachite-green and Hydrochloric Acid.*

The acid used was 0·0186N.

The value of r was taken as 11·0, the mean of eight results (limits 10·92—11·16) being 11·02.

Summary.

Expt.	Acid in c.c. = s.	No. of readings.	k_2+k_1s (decimal).	Diff.	k_2 (natural).	k_1 (natural).	$k_2s^{\frac{1}{3}}$.
20	20·00	16	0·0155	0·0005	0·0127	0·00115	0·0344
21	17·99	17	0·0149	0·0004	0·0130	0·00118	0·0341
22	16·02	18	0·0144	0·0004	0·0135	0·00123	0·0340
23	14·00	18	0·0130	0·0005	0·0132	0·00120	0·0318
24	12·46	13	0·0125	0·0005	0·0135	0·00123	0·0313
25	12·00	18	0·0123	0·0005	0·0135	0·00123	0·0310
26	10·05	19	0·0119	0·0006	0·0143	0·00130	0·0309
27	8·09	12	0·0127	0·0007	0·0169	0·00153	0·0338
28	6·03	15	0·0117	0·0008	0·0174	0·00158	0·0317
29	4·03	11	0·0147	0·0007	0·0248	0·00225	[0·0394]
						Mean =	0·0326

C. *Malachite-green Carbinol and Hydrochloric Acid.*

The carbinol was prepared in the same way as before, and the same method of calculation adopted, using the value $k_2s^{\frac{1}{3}} = 0·0326$.

Summary.

Expt.	Acid in c.c. = s.	No. of readings.	M.	Diff.	$Ms^{\frac{1}{3}}$.
30	14·13	11	0·0161	0·0011	0·094
31	12·96	15	0·0182	0·0005	0·100
32	12·01	20	0·0187	0·0010	0·098
33	10·06	16	0·0201	0·0016	0·094
34	9·07	18	0·0218	0·0011	0·095
35	8·18	15	0·0228	0·0017	0·092
36	7·05	20	0·0241	0·0015	0·089
37	4·03	16	0·0328	0·0021	[0·083]
				Mean =	0·095

D. *Malachite-green and Nitric Acid.*

Acid, 0·0212-normal.

The value of the equilibrium constant $r = \frac{x}{A-x}s$ was taken as 8·90, the mean of thirteen results (8·69—9·16) being 8·92.

Summary.

Expt.		Acid in c.c. = s.	No. of readings.	k_2+k_1s (decimal).	Diff.	k_2 (natural).	k_1 (natural).	k_1s.
38	*a.*	11·95	9	0·0131	0·0005	0·0129	0·00145	0·0295
	b.	11·95	16	0·0131	0·0004	0·0129	0·00145	0·0295
39	*a.*	10·40	9	0·0118	0·0005	0·0125	0·00141	0·0274
	b.	10·40	13	0·0117	0·0008	0·0124	0·00139	0·0271
40		8·00	9	0·0115	0·0005	0·0140	0·00157	0·0279
41		6·21	9	0·0115	0·0005	0·0156	0·00175	0·0287
42	*a.*	6·05	9	0·0119	0·0005	0·0163	0·00183	0·0297
	b.	6·05	10	0·0121	0·0007	0·0166	0·00187	0·0303
43	*a.*	3·99	12	0·0119	0·0005	0·0189	0·00213	0·0300
	b.	3·99	11	0·0117	0·0009	0·0186	0·00209	0·0295
							Mean =	0·0289

E. *Malachite-green Carbinol and Nitric Acid.*

Expt.	Acid in c.c. = s.	No. of readings.	M.	Diff.	$Ms^{\frac{2}{3}}$.
44 *a.*	16·00	12	0·0134	0·0005	0·0851
b.	16·00	10	0·0136	0·0006	0·0864
45 *a.*	11·80	12	0·0162	0·0007	0·0840
b.	11·80	12	0·0165	0·0014	0 0855
46	9·91	16	0·0179	0·0010	0·0826
47 *a.*	7·83	14	0·0205	0·0014	0·0808
b.	7·83	12	0·0208	0·0008	0·0820
48 *a.*	5 51	14	0·0271	0·0014	0·0846
b.	5·51	14	0·0275	0·0013	0·0858
49 *a.*	4·00	12	0·0310	0·0020	0·0781
b.	4·00	12	0·0316	0·0011	0·0796
50 *a.*	0·97	15	0·1035	0·0055	[0·1014
b.	0·97	15	0·1030	0·0070	0·1009]
				Mean =	0·0830

III. *Comparison of Results.*

In order to compare the various constants obtained, they must be referred to the common standard of a normal acid or alkaline solution.

(1) Reaction with alkali.—If N is the normality of the alkali used, the mean value of $\frac{K}{n}$ gives the value of the constant K for a solution containing 1 c.c. of this alkali in 50. Hence the velocity (K_n) in a normal solution of alkali is $\frac{K}{n} \times \frac{50}{N}$. With regard to the calculation of this constant in our previous paper, we regret that it contains two numerical errors. The strength both of the sodium hydroxide and of the hydrochloric acid there used are stated to be greater than they really were. The former was actually $0·0241N$, and the latter $0·0203N$. Also, in calculating K_n from our results for comparison with those of Hantzsch and Osswald, the value used was in decimal instead of natural logarithms. The correct value is obtained thus: The mean value of $\frac{K}{n}$ for brilliant-green is in decimal logarithms 0·0196, and in natural logarithms, 0·0453. Hence for normal alkali it is $0·0453 \times \frac{50}{0·0241} = 94·2$. As we have shown (*loc. cit.*), the velocity deduced from Hantzsch and Osswald's experiments (*Ber.*, 1900, **33**, 278) by Gerlinger (*ibid.*, 1904, **37**, 3958) when corrected to 21·2° in accordance with their determination of the temperature-coefficient in similar cases, is 42·3. Our result is therefore more than twice as great. Now these calculations are based on the assumption that the true dye-base (the coloured quaternary hydroxide) can be regarded as fully ionised at all the dilutions examined, and hence the concentration of the ions can be taken as equal to that of the dye as a whole.

If so, the change of the dye-base into the carbinol in Hantzsch and Osswald's experiments is bimolecular, whilst in our case, where the concentration of hydroxyl does not alter, it is unimolecular, the constant being proportional to the amount of alkali used. But it is quite possible that whilst this assumption holds in our experiments (where $V = 100,000$ or more), it is no longer true at the greater concentrations (beginning at $V = 256$) investigated by Hantzsch and Osswald. If the difference in the two determinations is due to this cause, then since the velocity deduced from the conductivity measurements is 44·9 per cent. of that calculated from our results, it follows that at $V = 256$ the concentration of the cation of the dye (or of hydroxyl) is $\sqrt[2]{0{\cdot}449} = 0{\cdot}670$ of that of the dye as a whole; that is, that the dye-base is only 67 per cent. dissociated. Nor does this result seem improbable if we consider that this is a higher degree of dissociation than was found at the same dilution by Bredig (*Zeitsch. physikal. Chem.*, 1894, **13**, 299) for any secondary or tertiary amine. A base which is 67 per cent. ionised at $V = 256$ has a constant $k = 0{\cdot}00531$, whilst for diethylamine (the strongest of Bredig's secondary bases) $k = 0{\cdot}00126$, and for triethylamine (the strongest tertiary base) $k = 0{\cdot}00064$.

We may therefore conclude that the discrepancy between Hantzsch and Osswald's results and ours is due to the dye-base not being wholly ionised at the greater concentration.* If this is so, the bimolecular formula applied by Gerlinger to their numbers cannot strictly hold; and this may account for the large and unexplained corrections which he was compelled to make in the conductivity measurements in order to bring them under this formula.

If this value of the dissociation constant of the dye-base is correct, it is not completely ionised even at the dilutions which we have used, and hence our results should show a falling off of K/n with increase of n. The tables given for brilliant-green in our previous paper, and for malachite-green in this paper, indicate that such a falling off does occur, although it is scarcely beyond the limits of experimental error, and is much less than that calculated on the basis of $k = 0{\cdot}00531$. This may be taken as a proof that the value of k derived from the comparison with Hantzsch and Osswald's results is too small, and that the dye-base is really more completely ionised than we have supposed. In view of the various assumptions and approximations which the comparison necessitated, it is very probable that this is the case.

(2) Reaction of the dye-salt and carbinol with acid.—For the equilibrium constant r we have:

$$r = \frac{x \, . \, s}{A - x},$$

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* An analogous instance, of a much weaker base, is described in the following paper.

where s is the number of c.c. of acid of normality N in 50 c.c. of the solution. The actual normality of the acid is thus $sN/50$, and the value of r must be multiplied by $N/50$ to give the normal constant r_n.

The constants k_1 and k_2 of the reversible formation of the acid salt from the dye-salt are given by

$$\frac{dx}{dt} = k_1 s + k_2(A - x).$$

Hence the value of k_2 for any particular strength of acid is unaltered. But the expression which was found to be independent of the acid, $k_2 s^{\frac{1}{3}}$, must be referred to a normal acid, and therefore becomes

$$k_{2n} = k_2 s^{\frac{1}{3}} \times \left(\frac{N}{50}\right)^{\frac{1}{3}},$$

while k_{1n} is obtained by dividing k_{2n} by r_n.

In the same way the carbinol constant M is itself independent of the units in which the acid is measured; but the constant expression $Ms^{\frac{2}{3}}$ becomes

$$M_n = Ms^{\frac{2}{3}} \times \left(\frac{N}{50}\right)^{\frac{2}{3}}.$$

The normal values of the constants so determined are given in the following table. Those obtained for the unsubstituted diaminotriphenylcarbinol in the work described in the following paper are added for the sake of comparison.

		Brilliant-green (tetraethyl-).	Malachite-green (tetramethyl-).	Diaminotri-phenylcarbinol.
Alkali	K_n	94·2	87·3	—
Acid	r_n HCl	0·00390	0·00409	0·0080
	r_n HNO_3	0·00483	0·00377	—
	k_{2n} HCl	0·00244	0·00234	0·00355
	k_{2n} HNO_3	0·00288	0·00217	—
	k_{1n} HCl	0·626	0·572	4·44
	k_{1n} HNO_3	0·596	0·576	—
	M_n HCl	0·000428	0·000489	0·00157
	M_n HNO_3	0·000464	0·000474	—

This comparison shows that neither the replacement of the four ethyl by methyl groups, nor the substitution of nitric for hydrochloric acid, makes any considerable difference in the constants. The first of these results was to be expected; but the second, the fact that the values with nitric and hydrochloric acids in no case differ by as much as 25 per cent., is certainly remarkable.

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XCIX.—*The Rate of Reaction of the Triphenylmethane Dyes with Acid and Alkali. Part III. Diaminotriphenylcarbinol.*

By Nevil Vincent Sidgwick and Albert Cherbury David Rivett.

The rates of change of diaminotriphenylcarbinol and its salts in presence of acid and alkali were investigated by the method described in the preceding paper.

The substance was prepared according to the directions given by Baeyer and Villiger (*Ber.*, 1904, **37**, 2860). We are indebted to Mr. D. Ll. Hammick, Demy of Magdalen College, for kindly carrying out this preparation. The dye was purified by repeated recrystallisation, first as the methyl ether, and then as the hydrochloride, the salt which was actually employed.

Of this salt a *N*/500 solution was prepared by dissolving 0·308 gram in 500 c.c. of water. The working solution (*N*/12,500) was prepared by diluting 10 c.c. of the first solution to 250, and of this, 5 c.c.* were taken for each experiment and made up in the tube of the tintometer to 50 c.c., so that the actual concentration of the dye in each case was *N*/125,000.

The salts of diaminotriphenylcarbinol are reddish-purple in strong solution, and pale pink at the highest dilutions employed. They are rather less deeply-coloured than those of brilliant-green and malachite-green. As regards the ease of measurement, there is no doubt that this pink dye is a greater strain on the observer than the greens. The accuracy of the measurements is, on the whole, nearly, if not quite, as great, but the liability to occasional large errors, which may always occur with this method, but which can be eliminated by a repetition of the measurements, or by comparison with other results, is greater with a pink than with a green solution.

The investigation may be divided, as before, into three parts:

(1) Action of alkali on the dye-salt.
(2) Action of acid on the dye-salt.
(3) Action of acid on the carbinol.

I.—*Action of Alkali on the Dye-salt.*

In the case of this dye, the rate of formation of the carbinol is so great that its measurement is attended with some difficulty. It was found necessary to use an alkali solution not stronger than *N*/500, in spite of the errors which this high dilution must cause, especially through the absorption of traces of carbon dioxide, and to make the observations as quickly as possible. If the adjustments of the tintometer to equality of tint are made by one observer, while the heights of the liquid are read and recorded by the other, it is possible with practice to take at least two readings a minute.* The range of observation can also be extended by taking twice the usual quantity (10 c.c.) of the working solution, and in some experiments this was done. The initial readings are always less trustworthy, and the reaction being unimolecular, the calculation can be begun at any point in the series. When the larger quantity of dye is used, these initial stages take place outside the range of the tintometer.

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* In certain cases, twice this quantity of the working solution was used.

The alkali used was 0·00198*N*-barium hydroxide. The temperature was, in all cases, 21·2°. The times were read to the nearest 5 seconds.

The velocity constant K is calculated according to the unimolecular equation

$$K = \frac{1}{t} \log \frac{A}{x},$$

A being the concentration (height of the balancing column in the tintometer) of the dye-base at time 0, and x the concentration at time t.

The actual depth of colour at the moment of adding the alkali was about 10 cm. where 5 c.c. were used, and about 20 cm. where 10 c.c. were used.

Summary

Expt.	Alkali in c.c.	No. of readings.	K (obs.).	Diff.*	K (calc.).†
1	0·72	13	0·098	0·008	—
2	0·88	10	0·096	0·006	—
3	1·67	11	0·089	0·005	—
4	1·79	8	0·101	0·013	—
5	2·13	10	0·107	0·007	—
6	3·11	6	0·116	0·009	—
7	3·70	7	0·114	0·008	0·102
8	3·90	10	0·125	0·009	0·106
9	3·98	6	0·123	0·006	0·107
10	6·10	9	0 143	0·003	0·143
11	7·94	12	0·165	0·015	0·167
12	9·83	9	0·184	0·011	0·187
13	11·68	7	0·214	0·015	0·204
14	15·02	6	0·239	0·011	0·227

* This column gives the maximum departure of any observed value of K from the mean.

† The basis of this calculation is given later.

In the case of brilliant-green and malachite-green, it was found that the reaction was unimolecular for any given quantity of alkali, and that the constant so obtained was approximately proportional to the amount of alkali taken, that is, that the rate of formation of the carbinol was proportional to the product of the concentrations of the cation of the dye-base (as this might be assumed to be practically entirely dissociated) and the hydroxyl ion. Since the concentration of the undissociated dye-base must, by Ostwald's law, be proportional to this same product, these results are to be expected if the carbinol is formed either from these two ions or from the undissociated dye-base, or from both.

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* In most of the experiments, the whole change took less than five minutes.

In the present case, whilst the unimolecular formula gives concordant results in each experiment, it will be seen that the constant increases much more slowly than the alkali, an increase in the latter from 0·9 c.c. to 15 c.c. raising the constant less than two and a-half times. Now this unsubstituted dye is a much weaker base than its tetra-alkyl derivatives, for its hydrochloride is considerably hydrolysed in dilute solution, as will be shown later. We are therefore not justified in assuming that it is wholly dissociated. Let k_1 be its dissociation constant, A the total concentration of the base, x the fraction ionised, and a the concentration of the alkali. Then by Ostwald's law

$$k_1 = \frac{C_{\text{cation}} \times C_{\text{OH}}}{C_{\text{undiss. base}}}$$

$$= \frac{A \cdot x \cdot a}{A(1-x)},$$

therefore $$k_1(1-x) = x \cdot a;$$

therefore $$x = \frac{k_1}{k_1 + a}.$$

If the carbinol is formed from the ions of the base, its rate of production will be

$$\frac{dy}{dt} = k_2 \times C_{\text{cation}} \times C^{\text{OH}},$$

$$= k_2 \cdot A \cdot x \cdot a$$

$$= k_2 \cdot a \cdot \frac{k_1}{k_1 + a} \cdot A \quad . \quad . \quad . \quad . \quad . \quad (1).$$

If it is formed from the undissociated base, the rate is

$$\frac{dy}{dt} = k_3 \times C_{\text{undiss. base}}$$

$$= k_3 \cdot (1-x) \cdot A$$

$$= k_3 \cdot \frac{a}{k_1 + a} \cdot A \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In any one experiment a is constant, and both (1) and (2) reduce to the form $A \times$ const. Hence the reaction in these circumstances should be unimolecular, as it was found to be, the observed constant K, since it is obtained by integrating the equation $\frac{dy}{dt} = K \cdot A$, being in the first case equal to $k_2 . a . \frac{k_1}{k_1+a}$ or $k_1 . k_2 . \frac{a}{k_1+a}$, and in the second to $k_3 . \frac{a}{k_1+a}$. As k_1 is a constant, we have in either case

$$K = \frac{a}{k_1+a} \times \text{const.}$$

It is obvious that if k_1 is very large, so that a may be neglected in comparison with it, this expression reduces to $\frac{a}{k_1} \times$ const.; that is, when the base is very strong (as in brilliant-green), K will be proportional to a, as was there found to be approximately the case. If k_1 is not very large, the increase of K will be less than that of a, and for any given value of k_1 this increase can be calculated. In the present case, the value of k_1 which gives the closest agreement with experiment is 0·0004, which is nearly twenty times the "apparent" dissociation constant of ammonia (0·000023) and a little less than that of methylamine (0·0005), while it is about a twelfth of that (0·0531) deduced for the tetraethyl compound (brilliant-green) in the preceding paper. The numbers given in the sixth column of the summary are calculated on this assumption, taking k_3 as 0·38. It will be seen that they agree very fairly with observation when more than 3 5 c.c. of alkali are used, that is, when the alkali is more than $N/7000$. When less alkali is used, the calculated values are much lower than the observed; for example, for 2·13 c.c., 0·066 instead of 0·107, and for 0·72 c.c., 0·025 instead of 0·098. At such dilutions there are obvious possibilities of error, but there would also seem to be some new factor concerned, perhaps connected with the hydration or ionisation of the second amino-group, which we are unable to take into account.

The question whether the carbinol is formed from the ions or from the undissociated base, or from both, is so far left open, and no conclusive answer can be given to it. But the following considerations make it probable that the reaction is due, at least in the main, to the undissociated portion. It was shown that the dissociation constant of the dye-base of brilliant-green is at least 0·00531 (it is probably considerably greater, but this value may be taken for the purpose of the calculation), and that the mean value of K in a solution of this dye containing 1 c.c. of 0·0241 N-alkali in 50 is 0·0196. If the reaction is due to the ions, then since

$$K = k_2 . a . \frac{k_1}{k_1+a}$$

therefore $$0{\cdot}0196 = k_2 \times 0{\cdot}000481 \times 0{\cdot}917;$$

therefore $$k_2 = 44{\cdot}5$$

referred to a normal alkali solution.

If the reaction is due to the undissociated part, we have

$$K = k_3 \times \frac{a}{k_1 + a};$$

therefore $$0{\cdot}0196 = k_3 \times 0{\cdot}083;$$

therefore $$k_3 = 0{\cdot}236.$$

In the case of the diamino-compound we have seen that if it is the undissociated part which reacts, $k_3 = 0{\cdot}38$. If it is the ions, then since

$$K = 0{\cdot}143 \text{ with } 6{\cdot}10 \text{ c.c. alkali},$$

therefore $$0{\cdot}143 = k_2 \times 0{\cdot}000242 \times 0{\cdot}0004 \div 0{\cdot}000642;$$

therefore $$k_2 = 948{\cdot}0.$$

Hence, if the carbinol is produced from the undissociated part of the base, the reaction velocity of the unsubstituted dye is $0{\cdot}38 \div 0{\cdot}236 = 1{\cdot}6$ times as great as that of the tetraethyl derivative, whereas if it is formed from the ions it is $948 \div 44{\cdot}5 = 21{\cdot}3$ times as great. Now we have shown (see table at the end of the preceding paper) that the absence of the alkyl groups increases the velocity with which the dye reacts with acids, but on the average not more than 3 to 4 times. It is therefore unlikely that the velocity constant of the carbinol formation should be increased more than twenty-fold, and we may thus conclude that it is the undissociated part which undergoes the change into the carbinol, and not the ions. The same conclusion is indicated by the work of Dimroth (*Annalen*, 1904, **335**, 1) on the triazoles, and that of Walker and Kay (Trans., 1897, **71**, 489) on the conversion of ammonium cyanate into carbamide; in both cases it was found that the change was much more rapid in alcohol (where the dissociation must be less) than in water.

II.—*Action of Acid on the Dye-salt.*

In the case of brilliant-green and malachite-green, any addition of acid, however small, to the solution of the dye-salt causes a diminution of colour, owing to the formation of the acid salt. But with the unsubstituted dye a very small addition of acid causes an increase of colour, whilst a further addition makes the colour less again. These changes are not instantaneous, but are complete in a few hours. The maximum colour is produced by adding about 0·17 c.c. of 0·0186N-hydrochloric acid to 50 c.c. of $N/125{,}000$ solution of the dye-salt, that is, when the acid is about $N/15{,}800$. This change is obviously due to the salt in this case being hydrolysed, and we should expect this dye to be a weaker base than its tetra-alkyl derivatives. The free base thus liberated will change over to a great extent into the colourless carbinol, which remains in solution, and hence the colour will diminish. The addition of a small quantity of acid will diminish the hydrolysis, and therefore increase the colour, while a larger addition will cause the colour to decrease again, owing to the formation of the acid salt in the usual manner.

In order to determine the amount of this increase of colour, four tubes were filled with 50 c.c. of the $N/125,000$ dye solution, and to two of them was added 0·17 c.c. of the acid. The tubes were kept for some hours at 21°, and then measured. The colour of the tubes to which no acid had been added was 10·39 and 10·21 cm.: mean 10·30. That of the other two was 13·99 and 13·80 cm.: mean 13·90. Thus the mean value of the maximum increase of colour is 35 per cent.

The solution to which this excess of acid has been added is still to some extent hydrolysed, whilst at the same time it must contain a certain amount of the acid salt. It can be shown that the amount of hydrolysis remaining is small. We may assume that the salt obeys the law of hydrolysis for the salt of a strong acid and a weak base, that is:

$$\frac{C_{\text{acid}} \times C_{\text{base}}}{C_{\text{salt}}} = H,$$

where H is the hydrolytic constant. The above measurements show that at a dilution of $V = 125,000$ about a third of the salt is hydrolysed. Hence

$$\left(\frac{1}{3V} \times \frac{1}{3V}\right) \div \frac{2}{3V} = H, \text{ or } H = \frac{1}{6V}.$$

The amount of acid added gives a strength of $N/15,800$. If x is the degree of hydrolysis after this addition, the concentration of the free base is x/V, whilst that of the salt, since x is small, may be taken as $1/V$. Therefore:

$$\left(\frac{1}{15,800} \times \frac{x}{V}\right) \div \frac{1}{V} = \frac{1}{6V}, \text{ or } x = 0·021,$$

that is, the remaining hydrolysis is about 2 per cent., and is almost within the limits of experimental error.

We have still to determine the amount of acid salt present in the liquid. As will be shown later, the equilibrium between dye-salt and acid salt in the presence of excess of acid is given (as in the previous cases) by the expression

$$\frac{C_{\text{dye-salt}}}{C_{\text{acid salt}}} \times C_{\text{acid}} = \text{constant};$$

and in the case of this dye, if the concentration of the acid is expressed in terms of the number of c.c. of the acid in 50 c.c. of the solution, the value of the constant is 2·15. Hence if A' is the colour of the solution when the whole is in the form of dye-salt, and

x its colour after 0·17 c.c. of acid has been added, then $A'-x$ corresponds with the amount of acid salt present, and we have

$$\frac{x}{A'-x} \times 0{\cdot}17 = 2{\cdot}15$$
$$A' = 1{\cdot}09x.$$

This enables us to determine the degree of hydrolysis more accurately. The mean value of the colour of the acidified solution was found to be 13·90 cm. Had no acid salt been formed, it would have been 13·90 × 1:09 = 15·2. This must be increased by 2·1 per cent. for the residual hydrolysis, giving 15·5 cm. The mean value in the absence of acid was 10·3 cm. Hence the fraction hydrolysed is $(15{\cdot}5 - 10{\cdot}3) \div 15{\cdot}5 = 0{\cdot}335$. From this we can calculate the strength of the base by means of Arrhenius' equation (compare Walker, *Zeitsch. physikal. Chem.*, 1900, **32**, 138):

$$\frac{x^2}{(1-x)V} = \frac{K_w{}^2}{k},$$

where x is the hydrolysed fraction of the salt, K_w the dissociation constant of water (about 1×10^{-7} at 21°), and k that of the base. This gives $k = 7{\cdot}5 \times 10^{-9}$.

The value obtained for the dissociation constant of the dye-base from the alkali experiments was 4×10^{-4}: about 50,000 times as large. But it is clear that the hydrolysis of the salt solution depends, not on the strength of the dye-base, but on that of the system (dye-base $\rightleftarrows$ carbinol) at equilibrium. When the solution is allowed to stand, as in the measurement of hydrolysis, the dye-base which is at first liberated must change over into the carbinol, and this will cause further hydrolysis, whilst the determination of the strength of the dye-base from its rate of change in presence of alkali indicates the basicity of this form itself. We have, in fact, here a real case of the "abnormal hydrolysis" of a pseudo-base, and the objections which Kauffmann (*Zeitsch. physikal. Chem.*, 1904, **47**, 618) has brought against this phenomenon in general do not apply to this case, since they were based on the assumption that equilibrium was attained. The calculation of the proportions at equilibrium of the dye-base and the carbinol is rendered difficult, if not impossible, by the fact that the latter is itself a base (although weaker than the dye-base), and hence will combine with some of the hydrochloric acid.

For the calculation of the velocity experiments with acid, it is necessary to know the initial value of the colour when the substance is present wholly as dye-salt. In order to eliminate hydrolysis, the working solution (N/12,500) was made up with 34 c.c. of 0·0186N-acid to the litre. For each experiment, 5 c.c. of this solution (containing 0·17 c.c. of acid) were placed in the tintometer tube, and so much water added as with the acid to be used would make up 50 c.c. The tube was allowed to stand several hours at 21° to attain equilibrium, and its colour read. From the observed value (A), the corrected value (A'), allowing for the amount of acid salt present, can be obtained by means of the formula given above. The correction varies slightly according to the volume of the liquid, as this affects the strength of the acid.

The quantity of acid required to make up the 50 c.c. was then added from a burette, and a series of readings taken at known intervals of time.

The amount of acid salt formed at equilibrium was determined by measuring the colour after the solution had remained at 21° for at least five hours, and in many cases overnight. If A' is the corrected initial value, and x the final reading, the constant r is calculated from the equation:

$$\frac{x \times s}{A' - x} = r.$$

The mean value obtained for r from twenty-one experiments, in which the acid varied from 1·22 c.c. to 10·10 c.c., and the extreme limits of r were 2·06 and 2·24, was 2·15.

This constant represents the ratio of the velocities k_1 and k_2 in the reversible reaction:

$$\text{dye-salt} + \text{HCl} = \text{acid salt},$$

when $$k_1 \times C_{\text{acid}} \times C_{\text{dye-salt}} = k_2 \times C_{\text{acid salt}}.$$

The fact that at the beginning of the experiment the solution contains a small quantity of acid salt introduces a slight modification into the integration, which takes the form

$$\log \frac{(s - s_1) \,.\, A \,.\, r}{(r+s)(r+s_1)} - \log\left(x - \frac{r \,.\, A}{r+s}\right) = t(k_2 + k_1 s),$$

where s_1 is the amount of acid (0·17 c.c.) present in the solution to begin with, and s the total quantity present when the reaction starts. The results of the velocity experiments are summarised in the following table:

Summary.

Expt.	Acid in c.c. $= s$.	No. of readings.	$k_2 + k_1 s$ (decimal).	Diff.	k_2 (natural).	k_1 (natural).	$k_1 s^{\frac{1}{2}}$.
15	9·69	17	0·140	0·007	0·0585	0·0272	0·0847
16	9·04	20	0·139	0·007	0·0615	0·0286	0·0860
17	8·20	10	0·135	0·010	0·0645	0·0300	0·0859
18	7·46	18	0·136	0·008	0·0701	0·0326	0·0890
19	7·29	19	0·132	0·006	0·0692	0·0322	0·0869
20	5·06	17	0·115	0·007	0·0791	0·0368	0·0828
21	2·86	14	0·111	0·011	0·1099	0·0511	0·0864
22	2·80	18	0·105	0·004	0·1051	0·0489	0·0818
23	2·30	12	0·115	0·006	0·1281	0·0596	0·0904
24	1·81	15	0·106	0·005	0·1324	0·0616	0·0829
25	1·56	9	0·109	0·007	0·1456	0·0677	0·0846
						Mean =	0·0856

It will be seen that the value of $k_1s^{\frac{1}{2}}$, and hence also that of $k_2s^{\frac{1}{2}}$, remain approximately constant. In the case of the tetra-alkyl derivatives, brilliant-green and malachite-green, it was found that the expression $k_2s^{\frac{1}{2}}$ was practically independent of s so long as this was not too small. It is probable that both these expressions are merely approximation formulæ. The fact that in all cases the velocity constant diminishes as the acid increases suggests that it is the hydrolysed portion of the salt that reacts, but the laws governing the hydrolysis in such cases as these are too complicated to be worked out until we have more knowledge of the behaviour of the simpler compounds, and especially of the monoamino-derivatives.

III.—*Action of Hydrochloric Acid on the Carbinol.*

The reactions here are the same as in the case of brilliant-green and malachite-green, and the velocity constant M can be calculated from the equation given in the preceding paper (p. 892), using the values $k_1s^{\frac{1}{2}} = 0·0856$ and $k_2 = k_1 \times 2·15$. Mr. Moseley's graphic method (described in the last paper) was employed for solving the equation.

The carbinol solution was prepared as follows. Five c.c. of the working solution (N/12,500, with 34 c.c. of acid per litre) were placed in the tube and water added. After the tube had remained for some hours at 21°, the colour A was read, from which A' was calculated as before. Then a small quantity (about 0·35 c.c.) of N/50-barium hydroxide was run in, and the solution left to stand. The alkali being in excess, the colour practically vanishes after half an hour, and the carbinol solution is ready. The required amount of acid was then added, and the readings taken. For the purpose of the calculation, the acid used is, of course, corrected for the small excess of alkali employed.

Summary.

Expt.	Acid in c.c. $= s$.	No. of readings.	M.	Diff.	$Ms^{\frac{1}{2}}$.
26	0·56	9	0·460	0·019	0·312
27	0·66	11	0·389	0·014	0·295
28	0·91	11	0·367	0·010	0·345
29	1·18	13	0·290	0·009	0·324
30	1·36	19	0·257	0·009	0·316
31	1·47	18	0·253	0·008	0·330
32	1·83	10	0·207	0·004	0·310
33	2·03	10	0·184	0·014	0·295
34	2·42	11	0·163	0·009	0·294
35	2·45	12	0·163	0·008	0·296
36	2·95	12	0·142	0·006	0·292
37	3·14	12	0·141	0·010	0·302
38	3·73	11	0·114	0·007	0·274
39	4·23	11	0·107	0·005	0·280
40	4·58	13	0·101	0·005	0·279
				Mean =	0·303

This shows that, as with brilliant-green and malachite-green, the the value of $Ms^{\frac{2}{3}}$ is practically independent of s.

The values of r, k_1, k_2, and M for normal acid are given at the end of the previous paper, for comparison with those obtained for the other dyes. It will be seen that k_1 is about seven times, k_2 1·5 times, and M three times, as great as with the tetra-alkyl compounds. The velocity of reaction with alkali (formation of the carbinol) is, as has already been explained, about 1·6 times as great if we suppose it to be due to the undissociated portion of the dye-base, and twenty-one times as great if it is due to the ions.

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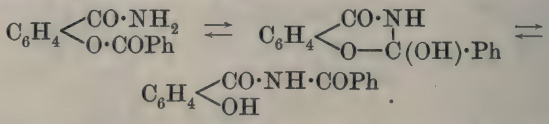
C.—*Labile Isomerism Among the Acylsalicylamide, Acylhydroxyamine, and Phenylbenzometoxazine Groups.*

By ARTHUR WALSH TITHERLEY and WILLIAM LONGTON HICKS.

THE peculiar rearrangement phenomena which have been recorded in the acylsalicylamide group by the authors (Trans., 1905, **87**, 1207), McConnan and Titherley (Trans., 1906, **89**, 1318), and McConnan (Trans., 1907, **91**, 196) have been shown by McConnan and Titherley to be intelligible on the assumption that an intermediate unstable cyclic hydroxymetoxazone is produced; and, for example, the mechanism of the reversible change of *O*-benzoylsalicylamide to *N*-benzoylsalicylamide was explained thus:



$$C_6H_4{<}{\begin{matrix}CO{\cdot}NH_2\\O{\cdot}COPh\end{matrix}} \rightleftarrows C_6H_4{<}{\begin{matrix}CO{\cdot}NH\\O{-}C(OH){\cdot}Ph\end{matrix}} \rightleftarrows C_6H_4{<}{\begin{matrix}CO{\cdot}NH{\cdot}COPh\\OH\end{matrix}}.$$

Auwers (*Ber.*, 1905, **38**, 3256), however, explained this change by free wandering of the acyl group, and later published a further criticism (*Ber.*, 1907, **40**, 3506) of the cyclic theory of McConnan and Titherley. The object of the present paper is to deal with Auwers' criticism, and to describe the behaviour of phenylbenzometoxazone with phosphorus pentachloride, which has been recently investigated.

It is admitted by McConnan and Titherley (*loc. cit.*) that Gerhardt's compound (m. p. 208°) must be given the *N*-benzoyl formula as first urged by Auwers, and they have directly proved this by the fact that it yields the *O*-methyl ether, $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}NHBz$ with diazomethane. Further, it must be admitted that the so-called "coumarazines" of Cebrian (*Ber.*, 1898, **31**, 1592), in which a cyclic metoxazone structure appeared similar to that under discussion, can have no bearing on the problem, since Titherley and Marples (Trans., 1908, **93**, 1933), in repeating Cebrian's work, have shown that his supposed cyclic derivatives possess an open-chain structure.

Auwers' theory of acyl wandering is based on his comprehensive study of rearrangement phenomena among acylated ortho-aminophenols, hydroxybenzylamines, and related derivatives (*Ber.*, 1900, **33**, 1923; *Annalen*, 1904, **332**, 159; *Ber.*, 1904, **37**, 2249, 3903, 3915, 3920). He has shown that *O*-acyl-*o*-aminophenols, $OAc\cdot C_6H_4\cdot NH_2$, and *O*-acyl-*o*-hydroxybenzylamines, $OAc\cdot C_6H_4\cdot CH_2\cdot NH_2$, are, in general, too unstable to exist, and that when attempts are made to prepare them, the *N*-acyl isomerides usually result. In a few cases, however, such *O*-acyl derivatives are capable of existence. Söderbaum and Widman (*Ber.*, 1889, **22**, 1665), and Paal and Bodewig (*Ber.*, 1892, **25**, 2961), have shown that *O*-acetyl-*o*-aminobenzyl alcohol,

$$CH_3\cdot CO\cdot O\cdot CH_2\cdot C_6H_4\cdot NH_2,$$

is capable of existence, and this has been fully confirmed by Auwers (*Ber.*, 1904, **37**, 2249). The *O*-acetyl derivative of *o*-nitro-*o*-hydroxyphenylbenzylamine, $OAc\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4\cdot NO_2$, has also been isolated (Paal and Härtel, *Ber.*, 1899, **32**, 2057), but the corresponding compounds with the nitro-group in the meta- and para-positions could not be obtained. Sufficient evidence has not yet been accumulated to account for the differences in stability of such *O*-acyl-derivatives, but the following facts are evident.

(1) The stability of *O*-acyl derivatives depends on the nature and orientation of substituent groups, and not on the nature of the acyl group. With regard to the latter, Auwers showed that heavy groups, like benzoyl and palmityl, underwent transport as readily as light groups, like acetyl, and that the negative character of the acyl group does not exert any sensible influence.

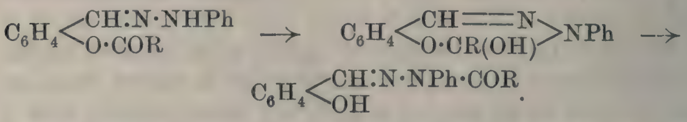
(2) The mobility of the acyl group in such *O*-acyl derivatives is confined to amino-*o*-hydroxy-derivatives, as was first indicated by Einhorn and Pfyl (*Annalen*, 1900, **311**, 34), who showed that no wandering occurred in the meta- and para-series of *O*-acylaminophenols.

As in all cases, the *N*-acyl isomeride appears to be the most stable. Auwers assumes that the nitrogen atom, by its basic nature, exerts an attractive influence on the acyl, thus providing the acyl group with a tendency to leave the *O*-position, and apart from the theory of free wandering it is probable that the nitrogen atom has some influence of this kind. But Auwers does not appear to have sufficiently considered the possibility of a cyclic mechanism in relation to his changes. In his earlier paper (*Annalen*, 1904, **332**, 159) it is true he considers the possibility of a ring formation in the first change of this kind noted by Böttcher (*Ber.*, 1883, **16**, 629), namely, the fact that *o*-nitrophenyl benzoate, $NO_2{\cdot}C_6H_4{\cdot}OBz$, yields on reduction *N*-benzoyl-*o*-aminophenol, $OH{\cdot}C_6H_4{\cdot}NHBz$, which might be due to the intermediate production of the cyclic derivative, $C_6H_4{<}\substack{N\\O}{>}C{\cdot}C_6H_5$; but he dismisses the idea of a cyclic mechanism, because in the rearrangement observed by Ransom (*Ber.*, 1900, **33**, 199), in which $CO_2Et{\cdot}O{\cdot}C_6H_4{\cdot}NH_2$ spontaneously changes to $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Et$, no such intermediate ring is possible.

Further, in the rearrangement of the *O*-acetyl derivative of *o*-hydroxybenzylaniline, $OAc{\cdot}C_6H_4{\cdot}CH_2{\cdot}NHPh$, Auwers states (*Annalen*, 1904, **332**, 162) that here no intermediate ring is possible. He thus overlooks the possibility of a hydroxy-cyclic derivative, as in the case of Ransom's compound $C_6H_4{<}\substack{NH\\O}{>}C{<}\substack{OEt\\OH}$, which by migration of the hydrogen atom might give $OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Et$, and in the case of his own compound, $C_6H_4{<}\substack{CH_2{\cdot}NPh\\O{-}C(OH){\cdot}CH_3}$, which similarly might give $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NAcPh$.

Such a cyclic mechanism, similar to that which the authors hold is involved in the acylsalicylamide rearrangements, would explain why the character and weight of the acyl group (which on a theory of simple wandering might be expected to exert a very marked influence) appear to have little or nothing to do with the changes. It would also explain why the changes are confined to the ortho-series, since it is only with ortho-derivatives that such cyclic systems are possible. If simple wandering occurs, it is difficult to see why a para-situated acyl group should not migrate, having regard to the close relation of ortho- and para-positions in such rearrangements as those shown by diazoamino-compounds, symmetrical hydrazines, etc.

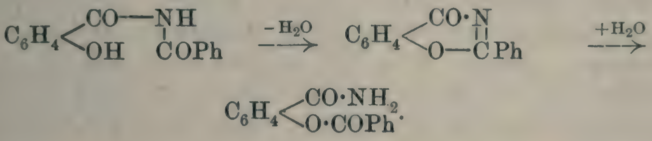
Auwers (*Ber.*, 1907, **40**, 3506) opposes the cyclic theory on the ground that seven-membered rings would be involved in the rearrangements which he has observed among *o*-hydroxyhydrazone derivatives, for example:



$$C_6H_4{<}\substack{CH{:}N{\cdot}NHPh\\O{\cdot}COR} \rightarrow C_6H_4{<}\substack{CH{=}N\\O{\cdot}CR(OH)}{>}NPh \rightarrow C_6H_4{<}\substack{CH{:}N{\cdot}NPh{\cdot}COR\\OH}.$$

This objection can scarcely be considered serious, having regard to the fact that the cyclic theory would postulate the formation of such seven-membered rings only as an unstable and intermediate phase in the rearrangement.

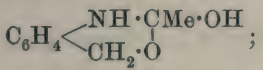
With regard to the acylsalicylamides, Auwers in his last paper (*Ber.*, 1907, **40**, 3506) admits the possibility of a cyclic mechanism in so far as the change from *N*-acyl- to *O*-acyl-salicylamide is concerned, although for the reverse change (*O*-acyl to *N*-acyl) he adheres to the theory of free wandering, at the same time accounting for the existence of *O*-acylsalicylamides (in contradistinction to the non-existence of *O*-acyl derivatives of the amines, $OH\cdot C_6H_4\cdot CH_2\cdot NHR$) by assuming that the more weakly basic nitrogen atom in the amide has a lower affinity for the acyl group than the nitrogen atom of the corresponding amines. No exception can be taken to the latter proposition, but the cyclic theory which he puts forward as an explanation of the change of acyl from *N*- to *O*- involves a loss of water for which there is no evidence in the change observed by McConnan and Titherley (*loc. cit.*), thus:



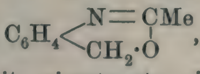
$$C_6H_4<\begin{matrix}CO—NH \\ OH \quad COPh\end{matrix} \xrightarrow{-H_2O} C_6H_4<\begin{matrix}CO\cdot N \\ O—CPh\end{matrix} \xrightarrow{+H_2O} C_6H_4<\begin{matrix}CO\cdot NH_2 \\ O\cdot COPh\end{matrix}.$$

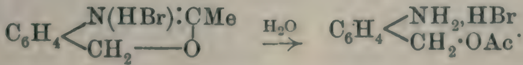
The loss and subsequent assimilation of water he states is due to the influence of acids; and this view of the rearrangement is based on the analogy of the change to the following important transformation which he has effected with the *N*-acetate of *o*-aminobenzyl alcohol $OH\cdot CH_2\cdot C_6H_4\cdot NHAc$ (*Ber.*, 1904, **37**, 2249).

When the latter in ethereal solution was treated with hydrogen chloride or bromide, a solid, crystalline precipitate was formed, which proved to be the salt of the ring compound,



$$C_6H_4<\begin{matrix}NH\cdot CMe\cdot OH \\ CH_2\cdot O\end{matrix};$$

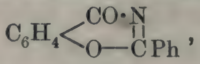
this, however, lost water on treatment with bases, forming the previously known ring,  $C_6H_4<\begin{matrix}N=CMe \\ CH_2\cdot O\end{matrix}$, "$\mu$-methylphenpentoxazole," which was identified by its picrate, etc. The unsaturated ring itself is stable, but its salts in aqueous solution absorb water, yielding the salt of the *O*-acetyl derivative of *o*-aminobenzyl alcohol:



$$C_6H_4<\begin{matrix}N(HBr):CMe \\ CH_2——O\end{matrix} \xrightarrow{H_2O} C_6H_4<\begin{matrix}NH_2,HBr \\ CH_2\cdot OAc\end{matrix}.$$

The free base is a colourless oil, which gradually changes into its isomeride, the *N*-acetyl derivative, $OH\cdot CH_2\cdot C_6H_4\cdot NHAc$.

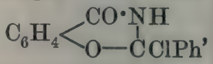
It is on these grounds that Auwers, in the acylsalicylamide group, assumes in the change *O*-acyl $\longrightarrow$ *N*-acyl a free wandering of the acyl, whilst in the change *N*-acyl ⟶ *O*-acyl (through the agency of acids) he assumes the formation of an intermediate unsaturated ring,



$$C_6H_4\begin{matrix}\diagup CO\cdot N \\ \diagdown O—CPh\end{matrix},$$

similar to that which he obtained. The transformation of *N*-benzoylsalicylamide to *O*-benzoylsalicylamide is effected by boiling with pure acetic acid, which may (although improbably) act as a dehydrating agent and so produce this hypothetical ring compound, but this view is rendered unlikely, since other similar changes (for example, that of *N*-benzoyl-*O*-acetylsalicylamide into *O*-benzoyl-*N*-acetylsalicylamide, and this into an isomeride melting at 106°: see McConnan and Titherley, *loc. cit.*) may take place in the presence of pyridine, or even an inert solvent, and, moreover, it is not possible for water to be eliminated in such rearrangements. These circumstances, and especially the latter, strongly militate against Auwers' cyclic hypothesis. Perhaps, however, the most striking circumstance in favour of the intermediate existence of a hydroxymetoxazone ring is the fact established by one of the authors (Trans., 1907, **91**, 1419) that phenylbenzometoxazone on oxidation passes directly into *N*-benzoylsalicylamide.

Since a relation is thereby proved between a hydroxymetoxazone ring and an *N*-benzoylsalicylamide, whilst Auwers admits the possibility of a relation between a metoxazone ring (although unsaturated) and *O*-benzoylsalicylamide, it appears reasonable to assume that a cyclic mechanism may be applied to an acyl change in either direction.

In order to throw further light on the relation between phenylbenzometoxazone and *N*-benzoylsalicylamide, attempts have been made to isolate 2-chloro-2-phenylbenzometoxazone,  $C_6H_4\begin{matrix}\diagup CO\cdot NH \\ \diagdown O—CClPh\end{matrix}$, without success; but the behaviour of phenylbenzometoxazone with phosphorus pentachloride has given remarkable results. In the cold, using molecular proportions, simple replacement of the carbonyl oxygen by two chlorine atoms appears to take place without evolution of hydrogen chloride, forming 4 : 4-dichloro-2-phenylbenzometoxazine, which, however, has not yet been isolated. By taking two or more molecules of phosphorus pentachloride and warming in chloroform solution, hydrogen chloride is lost, and the hydrogen atom in the 2-position is replaced by chlorine,* thus yielding the 2 : 4-

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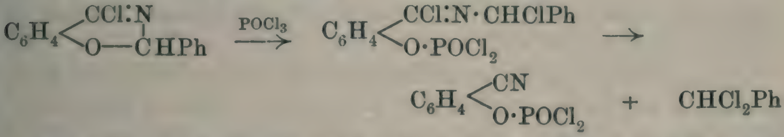
* This substitution, in which phosphorus pentachloride acts like a chlorinating agent, although unusual, finds a parallel in the chlorination of aromatic side-chains (although at higher temperatures) by Colson and Gautier (*Compt. rend.*, 1886, **102**, 690); in the chlorination of the aromatic ring, producing *p*-chloroanisole from

dichloro-derivative, which, however, immediately reacts with the phosphoryl chloride, yielding a bright yellow, crystalline powder. At the same time, a large quantity of the intermediate 4-chloro-derivative decomposes, forming benzylidene chloride and phosphorus derivatives of salicylonitrile under the influence of the phosphorus halide by-products; thus with phosphoryl chloride:

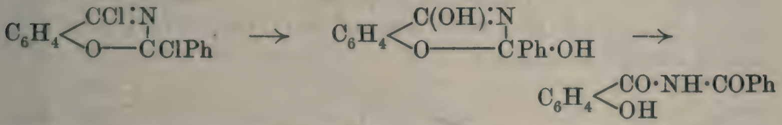


$$C_6H_4{<}\begin{matrix}CCl{:}N\\ \quad\;\; |\\ O{-}CHPh\end{matrix} \xrightarrow{POCl_3} C_6H_4{<}\begin{matrix}CCl{:}N{\cdot}CHClPh\\ O{\cdot}POCl_2\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CN\\ O{\cdot}POCl_2\end{matrix} + CHCl_2Ph$$

The yellow, crystalline solid, which is extremely unstable, was found to vary considerably in composition according to its mode of preparation and the proportion of phosphorus pentachloride used. Figures were obtained on analysis corresponding with the derivatives of dichlorophenylbenzometoxazine, $C_{14}H_9ONCl_2,POCl_3$ or

$$C_{14}H_9ONCl_2,PCl_5,$$

or mixtures of these, but the variation in composition does not sensibly affect the properties. With water, the yellow substance is instantly decomposed, yielding benzoylsalicylonitrile. *N*-Benzoylsalicylamide was expected, thus:



$$C_6H_4{<}\begin{matrix}CCl{:}N\\ \quad\;\; |\\ O{-}CClPh\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}C(OH){:}N\\ \qquad\;\; |\\ O{-\!-\!-}CPh{\cdot}OH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CO{\cdot}NH{\cdot}COPh\\ OH\end{matrix}$$

and a small quantity (from 1 to 5 per cent.) is usually produced, together frequently with a little salicylonitrile and benzoic acid; but when the yellow solid is dissolved in 98 per cent. sulphuric acid it is decomposed with evolution of hydrogen chloride, and gives a nearly quantitative yield of *N*-benzoylsalicylamide. Since benzoylsalicylonitrile is not converted into the latter by concentrated sulphuric acid, this remarkable difference in the behaviour of the yellow solid according to the mode of presentation of water appears to indicate a tautomeric behaviour of a very curious nature. The unexpected production of benzoylsalicylonitrile in the simple water decomposition led the authors to examine the behaviour of this substance with phosphorus pentachloride; they were surprised to find that although neither benzonitrile nor phenyl benzoate react under similar conditions, benzoylsalicylonitrile reacts with phosphorus pentachloride

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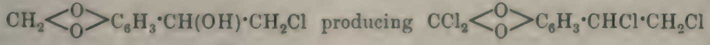
anisole, between 30° and 70° (Autenrieth, *Arch. Pharm.*, 1895, **233**, 31); and at 150—170°, in the chlorination of cyclic methylene esters like

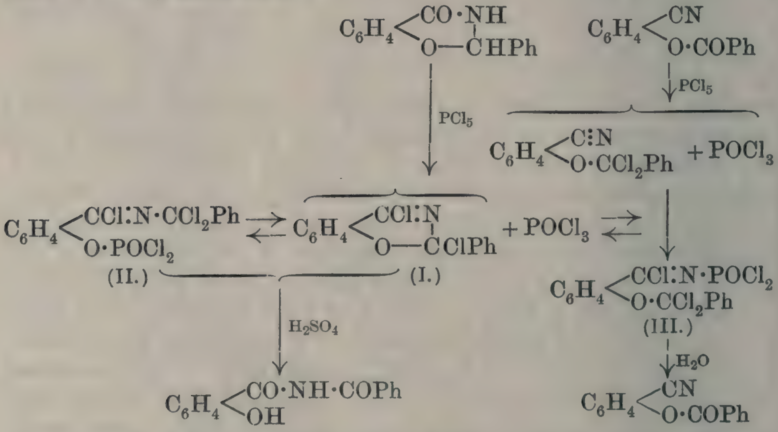


$$CH_2{<}\begin{matrix}O\\ O\end{matrix}{>}C_6H_3{\cdot}CH(OH){\cdot}CH_2Cl \text{ producing } CCl_2{<}\begin{matrix}O\\ O\end{matrix}{>}C_6H_3{\cdot}CHCl{\cdot}CH_2Cl$$

(Barger, Trans., 1908, **93**, 2081).

at 130°, yielding a bright yellow, crystalline solid, the properties of which are identical with those of the substance obtained from phenylbenzometoxazone. There can be no doubt as to the identity of the substance obtained from the two sources, although analyses revealed variations in the contents of phosphorus and chlorine, and indicated that whilst the substance obtained from benzoylsalicylonitrile is more frequently $C_{14}H_9ONCl_2,PCl_5$, that obtained from the metoxazone is usually $C_{14}H_9ONCl_2,POCl_3$.

Attempts to isolate the dichlorometoxazine, $C_{14}H_9ONCl_2$, free from phosphorus halides have failed, and it is evident that such phosphorus halides are an essential part of the structure, and that the yellow solid cannot be regarded as a double compound, as was at first supposed. It is probable that the phosphorus atom is linked to oxygen or nitrogen in the manner indicated in the alternative formulæ (II) and (III), taking the compound $C_{14}H_9ONCl_2,POCl_3$, but the relations observed appear to be intelligible only by attributing mobility to the groups ·CCl_2Ph and ·$POCl_2$, thus involving tautomerism, shown in the scheme below, analogous to that appearing in the acylsalicylamide group. The open-chain forms (II) and (III) are reversibly related, on this assumption, through the cyclic dichlorophenylmetoxazine (I). It is impossible at present to say whether the yellow solid, $C_{14}H_9ONCl_2,POCl_3$, is a mixture of (II) and (III), or one of these in a very labile form:

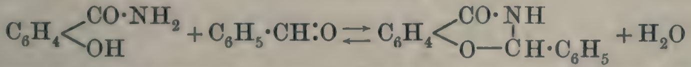


C6H4<CO·NH / O—CHPh
C6H4<CN / O·COPh
PCl5
PCl5
C6H4<C:N / O·CCl2Ph + POCl3
C6H4<CCl:N·CCl2Ph / O·POCl2
(II.)
C6H4<CCl:N / O—CClPh + POCl3
(I.)
C6H4<CCl:N·POCl2 / O·CCl2Ph
(III.)
H2SO4
H2O
C6H4<CO·NH·COPh / OH
C6H4<CN / O·COPh

A further study is being made of the chloro-derivatives in this group; in the meantime, however, it must be admitted that the results, so far, throw no fresh light on the general problem under discussion.

EXPERIMENTAL.

The phenylbenzometoxazone used in this investigation was prepared by a modified method of that given by Titherley (Trans., 1907, **91**, 1425), by which a considerably improved yield was obtained. A mixture of 50 grams of salicylamide and 50 grams of benzaldehyde in 150 c.c. of absolute ether was treated with 4 c.c. of concentrated alcoholic hydrogen chloride and heated to gentle ebullition in a reflux apparatus for four hours. The salicylamide, at first largely in suspension, gradually dissolved, and in about one and a-half hours a clear solution resulted, from which phenylbenzometoxazone soon began to separate in fine, silky needles. The contents of the flask eventually became nearly solid, and, after cooling, the mass of crystals was collected and washed with a little ether. In order to remove traces of salicylamide which were present, the crystals were digested for half an hour with cold dilute sodium hydroxide. The insoluble phenylbenzometoxazone was finally once recrystallised from boiling alcohol, and thus obtained perfectly pure (m. p. 169°). The ethereal filtrate in the above treatment contained large quantities of unaltered salicylamide and benzaldehyde, together with about 5 grams of phenylbenzometoxazone, which was recovered by evaporation. The total yield obtained was 60 grams, the theoretical quantity being 81 grams. The condensation under all conditions which have been tried is incomplete, and under most conditions a much smaller yield than the above is obtained. The reaction



$$C_6H_4{<}\begin{matrix}CO\cdot NH_2\\ OH\end{matrix} + C_6H_5\cdot CH{:}O \rightleftharpoons C_6H_4{<}\begin{matrix}CO\cdot NH\\ \quad\;\; |\\ O-CH\cdot C_6H_5\end{matrix} + H_2O$$

is a reversible one; and this has been shown experimentally to be the case, phenylbenzometoxazone, dissolved in benzene, ether, and other solvents, being largely decomposed in the presence of hydrogen chloride into salicylamide and benzaldehyde when moisture is admitted.

Action of Phosphorus Pentachloride on Phenylbenzometoxazone.

(*a*) *Without Solvent.*—Ten grams of phenylbenzometoxazone (1 mol.) and 20 grams of phosphorus pentachloride (2 mols.), intimately mixed, were heated at 80°, care being taken to exclude moisture. Hydrogen chloride was copiously evolved, but the evolution practically ceased after five minutes, when the contents of the flask had settled to a yellow oil with unchanged phosphorus pentachloride at the bottom. No phosphorus trichloride distilled over. On raising the temperature to 100°, a second reaction set in slowly, the liquid became turbid, and a bright lemon-yellow, crystalline solid began to form. The amount of the latter increased continually, and the temperature was raised to 140° and kept at this for forty-five minutes. Only traces of phosphoryl chloride distilled over, together with a little phosphorus trichloride. The bright yellow, crystalline solid in the flask, admixed with a considerable quantity of oil, was isolated by cooling and treating with pure benzene, which dissolved the oil. The yellow solid, after washing thoroughly with cold benzene and finally with ether, and removing adherent ether by means of air dried over phosphoric oxide, weighed 5 grams. It could not be crystallised from organic solvents without decomposing, but appeared to be a perfectly homogeneous pure compound. It was analysed by decomposing it cautiously in a closed vessel with water, by which hydrochloric and phosphoric acids were formed, together with benzoylsalicylonitrile, which was collected and weighed. The phosphoric acid was estimated by first precipitating as phosphomolybdic acid, and finally weighing as magnesium pyrophosphate, and the hydrochloric acid was estimated gravimetrically in the usual way; the two acids were also estimated volumetrically by titrating with *N*/10-sodium carbonate, using methyl-orange as indicator (with which 1 c.c. = 0·0031 gram P), and then titrating the resulting solution with *N*/10-silver nitrate, using potassium chromate (in larger quantities than usual) as indicator:*

1·0886 gave 0·530 benzoylsalicylonitrile, equivalent to 0·0333 N_2. N = 3·06.

0·2177 required 32·7 c.c. *N*/10-Na_2CO_3 and 27·5 c.c. *N*/10-$AgNO_3$, equivalent to 0·01612 P and 0·0976 Cl. P = 7·40; Cl = 44·8.

0·8708 gave 0·1848 $Mg_2P_2O_7$. P = 6·0.

$C_{14}H_9ONCl_2,POCl_3$ requires N = 3·27; P = 7·19; Cl = 41·13 per cent.

The benzene filtrate from the insoluble yellow solid contained a large quantity of benzylidene chloride, together with phosphorus derivatives of salicylonitrile. It was shaken in a machine with water for three hours, whereby soluble acid phosphorus derivatives of the nitrile were produced and extracted. The benzene solution was finally washed with alkali, dried, the benzene distilled off, and the resulting oil fractionated. It distilled chiefly at 200°, and was easily identified as benzylidene chloride. The weight, 5 grams, is equivalent to 7 grams of phenylbenzometoxazone, thus showing that about three-fourths of the molecules of the latter are completely ruptured in the production of the yellow phosphorus compound.

The aqueous solution obtained by shaking the benzene extract with water was strongly acid, and reduced silver nitrate. On careful neutralisation with sodium carbonate, it gave a pale yellow solution consisting of sodium salts of phosphorous- and phosphoric-acid derivatives of salicylonitrile. The solution was heated at 100° for two hours in order to hydrolyse these, when an oil separated in considerable quantity. After cooling, it was extracted with ether, and the ethereal solution, after drying and evaporating, left an oil smelling strongly of salicylonitrile, which, on standing in a vacuum, set to a crystalline mass. After draining on a porous plate and washing with benzene, the crystals melted at 91°, the yield being about 2 grams. The substance gave a characteristic ferric chloride reaction, and was easily identified as salicylonitrile (m. p. 98°). In some of the experiments, salicylamide was also found.

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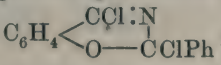
* The accuracy of this method, which is greater than would be anticipated, was checked by applying it to synthetic mixtures of known composition of sodium phosphate and hydrochloric acid, and to specially purified phosphoryl chloride. Good results were always obtained.

(*b*) *In Presence of Chloroform.*—A similar action takes place between phosphorus pentachloride and phenylbenzometoxazone in presence of chloroform at 60° to that which occurs at higher temperatures without solvent, but the reaction takes place more readily and leads to the production of a larger proportion of the yellow double compound. Moreover, the two stages in the reaction are not so well defined, inasmuch as the second chlorinating action sets in almost simultaneously with the first replacing action. Consequently, the yellow double compound is formed in moderate quantity even when molecular proportions of the original substances are taken, but the yield is much greater when 2 molecules of phosphorus pentachloride are used. Further, the composition of the resulting yellow solid varies according to the amount of pentachloride used, and by taking excess of the latter (3 molecules), the percentage of chlorine is raised almost to the figure corresponding with  $C_6H_4\left<\begin{array}{l}\mathrm{CCl{:}N}\\ \quad\ |\\ \mathrm{O{-}{-}CClPh}\end{array}\right.,PCl_5$, from which it appears that phosphoryl chloride and phosphorus pentachloride mutually replace each other according to their respective active masses.

4·4 Grams of phenylbenzometoxazone in 35 c.c. of chloroform (dried by phosphoric oxide) were treated with 8·2 grams of phosphorus pentachloride, and the mixture was heated to 60° for fifteen minutes. Hydrogen chloride was rapidly evolved, and the yellow solid formed, which, however, mostly dissolved in the hot chloroform. On distilling off the latter, bright yellow crusts remained, together with an oil, which was separated after cooling by treatment with pure benzene in the cold.

The insoluble yellow solid was first washed three times with cold benzene, and then, to remove any unaltered phosphorus pentachloride, it was washed three times by boiling with small quantities of benzene, in which, however, it was appreciably soluble, with evident dissociation. It was finally washed in a tube with ether, care being taken to exclude moisture. The yield was 2·5 grams.

A number of analyses of the substance, prepared in this way, were made. In some cases the substance was dried in a tube at 30° in a current of perfectly dry air, in other cases in an evacuated tube, care being taken to prevent leakage of atmospheric moisture.* The following results were obtained when 2 molecules of phosphorus pentachloride were used in the preparation:

(1) An unknown weight required 67·0 c.c. *N*/10-Na_2CO_3 and 56·0 c.c. *N*/10-$AgNO_3$. Ratio P : Cl = 1 : 5·1.
(2) 0·3620 gave 0·5947 AgCl. Cl = 40·64.
1·4480 „ 0·3132 $Mg_2P_2O_7$. P = 6·01.
(3) 1·0180 „ 1·6960 AgCl and 0·2200 $Mg_2P_2O_7$. Cl = 41·2; P = 6·03.

The following results were obtained when an excess of phosphorus pentachloride was used in the preparation:

(1) 1·7209 gave 0·4131 $Mg_2P_2O_7$. P = 6·70.
(2) 0·4302 required 68·8 c.c. *N*/10-Na_2CO_3 and 59·85 c.c. *N*/10-$AgNO_3$. P = 6·48; Cl = 49·3.
(3) 0·8313 gave 1·6284 AgCl. Cl = 48·46.
(4) 4·1564 required 67·55*N*-Na_2CO_3 and 568·25 c.c. *N*/10-$AgNO_3$. P = 8·01; Cl = 48·54.
(5) 2·0782 gave 0·5835 $Mg_2P_2O_7$. P = 7·84.
$C_{14}H_9ONCl_2,POCl_3$ requires P = 7·19; Cl = 41·13.
$C_{14}H_9ONCl_2,PCl_5$ „ P = 6·37; Cl = 51·10 per cent.

The high values for phosphorus in (4) and (5) were evidently due to small quantities of phosphorus pentachloride which had not been completely removed by benzene, the washing having probably been insufficient in these cases.

The properties of the yellow solid were substantially the same in all cases, but whilst samples with lower chlorine content gave an almost quantitative yield of benzoylsalicylonitrile on treatment with water, those richer in chlorine gave less, together with varying quantities of phosphoric derivatives of salicylonitrile and salicylamide. *N*-Benzoylsalicylamide was produced in all cases in small quantities (sometimes reaching 5 per cent.), but the chief product of decomposition by water was always benzoylsalicylonitrile, and this was found to hold, by direct treatment with water in presence of ether, benzene, and other solvents, as well as by decomposition with atmospheric moisture.

On dissolving in 98 per cent. sulphuric acid, the yellow solid gave large quantities of hydrogen chloride, and on diluting the solution with water, *N*-benzoylsalicylamide was formed as a thick, white precipitate, which, after recrystallising from alcohol, melted at 208°.

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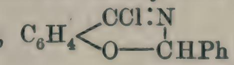
* Attempts made to dry the substance in an ordinary evacuated desiccator led to its complete decomposition, in twelve hours, to benzoylsalicylonitrile, which was shown to be due to leakage of atmospheric moisture. When special precautions are taken to exclude the latter, the yellow compound is unaltered in a vacuum.

The cold benzene washings obtained in the preparation of the yellow solid by the chloroform method contained a considerable quantity of benzylidene chloride, together with phosphorus chloro-derivatives, which were decomposed by water, yielding a mixture of salicylamide and phenylbenzometoxazone.

The hot benzene extract, obtained by boiling the washed yellow solid with benzene, also contained a phosphorus chloro-derivative, and on cooling, this was deposited in considerable quantity as an oil which slowly set to a pale yellow, crystalline mass. It was washed several times with light petroleum (b. p. 30—60°), and analysed by decomposing with water and estimating the phosphoric and hydrochloric acids volumetrically:

2·8860 required 33·1 c.c. N-Na_2CO_3 and 267 c.c. $N/10$-$AgNO_3$.
$P = 6·9$; $Cl = 32·84$.

As the ratio of $P : Cl = 1 : 4·17$, it appears likely that this crystalline solid of low melting point consists mainly of a double compound of the monochloro-derivative,  $C_6H_4\left<\begin{matrix}CCl{:}N\\ \vert\\ O{-}CHPh\end{matrix}\right.$, and phosphoryl chloride:

$C_{14}H_{10}ONCl,POCl_3$ requires $P = 7·8$; $Cl = 35·77$ per cent.

The substance, on treatment with water, yields an oil containing benzylidene chloride and benzaldehyde, from which, as well as from the aqueous solution, needles separate on standing. These were collected and found to consist in about equal proportions of a mixture of phenylbenzometoxazone (m. p. 168°) and salicylamide (m. p. 138°), which were readily separated by digesting with cold aqueous sodium hydroxide. The aqueous solution, moreover, from which the needles had separated contained a phosphoric acid derivative of salicylonitrile and salicylamide,* which were hydrolysed by heating in aqueous solution at 100°; on cooling, salicylonitrile (m. p. 85°) and salicylamide (m. p. 138°) were isolated by repeated extraction with ether and fractional crystallisation from benzene. From these observations it appears that the double compound of the monochloro-derivative exhibits a similar tautomeric behaviour to that of the dichloro-derivative:

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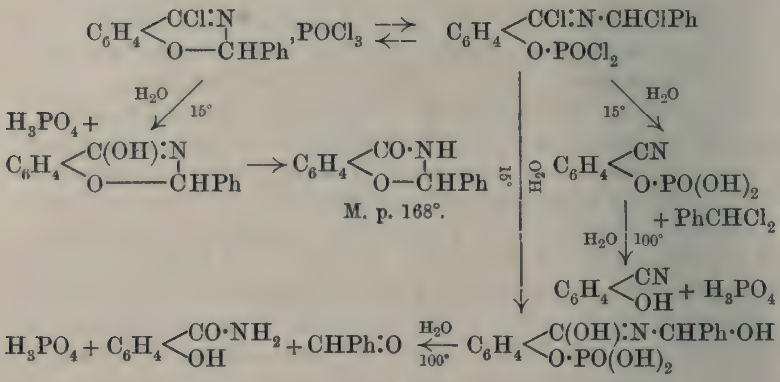
* The presence of such phosphoric acid derivatives in the aqueous solutions does not vitiate the above volumetric method used for determining phosphorus and chlorine, inasmuch as such derivatives containing the group $\cdot O \cdot PO(OH)_2$, like phosphoric acid, behave as a monobasic acid when methyl-orange is used as an indicator.



Action of Phosphorus Pentachloride on Benzoylsalicylonitrile.

In presence of boiling chloroform very slow action takes place between these substances, and without a solvent, first action sets in at about 100° without evolution of hydrogen chloride. At 130° the interaction is fairly rapid, producing the characteristic bright yellow solid identical in properties with that obtained from phenylbenzometoxazone at lower temperatures. A similar variation in composition was observed according to the proportion of phosphorus pentachloride used and the length of time of heating. The action was slow and incomplete even after two hours. The resulting yellow solid was washed thoroughly with benzene and finally with ether, and analysed in the manner previously described:

(1) 1·5850 gave 0·8000 benzoylsalicylonitrile, equivalent to 0·0502 N_2. N = 3·17.

(2) An unknown quantity required 33·0 c.c. *N*/10-Na_2CO_3 and 27·2 c.c. *N*/10-$AgNO_3$. Ratio P : Cl = 1 : 4·7.

(3) 0·5059 gave 1·0398 AgCl. Cl = 50·86.

(4) 2·0237 ,, 0·4763 $Mg_2P_2O_7$. P = 6·57.

$C_{14}H_9ONCl_2,POCl_3$ (ratio P : Cl = 1 : 5) requires N = 3·27 per cent.

$C_{14}H_9ONCl_2,PCl_5$ requires P = 6·37; Cl = 51·10 per cent.

Organic Laboratory,
University of Liverpool.

CI.—*The Colour and Constitution of the Alkyl Iodides of Cyclic Bases.*

By Charles Kenneth Tinkler.

It has previously been observed by various investigators that in a large number of cases the alkyl iodides of cyclic bases are coloured substances, the alkyl bromides slightly coloured, whilst the corresponding alkyl chlorides, hydrochlorides, and oxygen salts are colourless. In addition, it has been noticed that whilst these alkyl iodides give strongly-coloured solutions in chloroform, dilute aqueous or alcoholic solutions are colourless. In the case of the acridines, where the hydrochlorides and oxygen salts are themselves coloured, the solutions of the alkyl iodides in water and alcohol are similarly coloured, whilst the chloroform solutions are much darker in colour.

Decker (*Ber.*, 1904, **37**, 2938) explained the production of colourless solutions of these methiodides on the ground of ionisation, and he concluded that iodine joined to nitrogen, oxygen, or sulphur in an aromatic ring formed a chromophoric group, since the methiodides of cyclic bases were coloured, whilst substances such as diphenyldimethylammonium iodide, which do not contain nitrogen in a ring, were colourless.

In connexion with a spectroscopic investigation on the action of bases on *iso*quinoline methiodide, carried out at the suggestion of Dr. Decker on lines similar to those employed by Dobbie, Lauder, and Tinkler (Trans., 1903, **83**, 598) in their investigation on cotarnine, and by Dobbie and Tinkler on hydrastinine (Trans., 1904, **85**, 1005), it was found that yellow *iso*quinoline methiodide gave spectra in chloroform solution entirely different from those of the substance in aqueous or alcoholic solution. Similar results were obtained in the case of pyridine, quinoline, acridine, and phenylacridine methiodides. In a letter written to Dr. Decker by the author in November, 1907, it was suggested that these phenomena might possibly be explained otherwise than by ionisation.*

From the spectra of pyridine methiodide in chloroform it was seen that the absorption in the visible part of the spectrum showed some resemblance to that of potassium tri-iodide (Trans., 1907, **91**, 996), and it seemed possible that the colour of pyridine methiodide in chloroform solution might be due to the combination of two or more molecules of the substance by means of the iodine atoms, thus:

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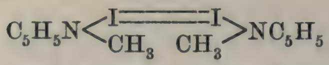
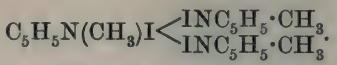
* An abstract from this letter has recently been published by Dr. Decker (*J. pr. Chem.*, 1909, [ii], **79**, 339).



$$C_5H_5N<\begin{matrix}I\!=\!=\!=\!I\\ CH_3\quad CH_3\end{matrix}>NC_5H_5$$



$$C_5H_5N(CH_3)I<\begin{matrix}INC_5H_5\cdot CH_3\\ INC_5H_5\cdot CH_3\end{matrix}.$$

Some determinations of the molecular weights of these methiodides were therefore undertaken, the results of which were communicated to Dr. Decker, but were not published.

In a recent paper, Hantzsch (*Ber.*, 1909, **42**, 68) draws the conclusion that the colour of these methiodides is due to polymerisation. Although my examination of these alkyl iodides is not yet complete, it is thought advisable to publish the results so far obtained.

In support of the view that colour is due to polymerisation, Hantzsch gives the following results of molecular-weight determinations of phenylacridine methyl halides by the ebullioscopic method.

	M.W. in		M.W. calculated.
	Alcohol.	Chloroform.	
Chloride	263	327 338	305·6
Bromide	341	424 421	350·0
Iodide	362	1161 1120	397·0
			397 × 3 = 1191·0

From these results it is seen that in chloroform the methiodide is termolecular, and that the bromide and chloride are slightly associated.

The following results were obtained by the author.

A. *Molecular Weights by the Ebullioscopic Method.*

Phenylacridine Methiodide in Chloroform.

			M.W.	
Substance.	Solvent.	E.	Found.	Calc.
0·4896 gram	45·1 grams	0·033°	1204	397
				397 × 3 = 1191

This result is in agreement with those given by Hantzsch, showing that the iodide in chloroform is termolecular.

Quinoline Methiodide in Alcohol.

			M.W.	
Substance.	Solvent.	E.	Found.	Calc.
1·3460 grams	15 grams	0·38°	277	271

At this concentration in alcohol this substance appears to be unimolecular. More probably, however, from the colour, the solution contains a mixture of polymolecular and unimolecular iodide, of which some of the latter is dissociated.

Owing to the slight solubility of the methiodides in chloroform, it is impossible to carry out other molecular-weight determinations in this solvent.

B. *Molecular Weights by the Cryoscopic Method.*

Determinations of molecular weights by the cryoscopic method, employing diphenylamine, have been undertaken, since the methiodides are insoluble or only sparingly soluble in the ordinary solvents used in such determinations. In some cases water was employed as solvent.

Pyridine Methiodide.—This substance was obtained colourless by crystallisation of alcohol (compare Hantzsch, *loc. cit.*). It is, however, strongly coloured when dissolved in chloroform or when molten.

Molecular Weight in Diphenylamine.

	Substance.	Solvent.	Δ*t*.	M.W. Found.	M.W. Calc.
(i)	0·3465 gram	24·38 grams	−0·15°	833	221
(ii)	0·5935 ,,	24·38 ,,	−0·24	892	221

The mixture so obtained is of a yellow colour.

In this case the substance appears to be in the quadrimolecular condition.

Molecular Weight in Water.

	Substance.	Solvent.	Δ*t*.	M.W. Found.	M.W. Calc.
(i)	0·2500 gram	18·88 grams	−0·22°	111	221
(ii)	0·4142 ,,	18·88 ,,	−0·34	119	221

In solution (i) the substance is apparently completely dissociated; both solutions are colourless.

Quinoline Methiodide: Molecular Weight in Diphenylamine.

	Substance.	Solvent.	Δ*t*.	M.W. Found.	M.W. Calc.
(i)	0·1434 gram	22·94 grams	−0·13°	423	271
(ii)	0·5709 ,,	22·94 ,,	−0·34	644	271

The solution is of a red colour. On the addition of alcohol and water, diphenylamine is precipitated, and a colourless solution of the methiodide is obtained.

In Water.

	Substance.	Solvent.	Δ*t*.	M.W. Found.	M.W. Calc.
(i)	0·2098 gram	15·26 grams	−0·19°	134	271
(ii)	0·6325 ,,	15·26 ,,	−0·46	166	271

In (i) the solution is colourless, and the substance is apparently completely dissociated.

In (ii) the solution is yellow, and probably contains some polymolecular modification with unimolecular, some of which is dissociated.

Phenylacridine Methiodide: Molecular Weight in Diphenylamine.

				M.W.	
	Substance.	Solvent.	Δ*t*.	Found.	Calc.
(i)	0·1300 gram	20·11 grams	−0·13°	438	397
(ii)	0·4070 ,,	20·11 ,,	−0·26	685	397

Both solutions apparently contain mixtures of unimolecular and polymolecular modifications.

From these results it appears that the substances are polymerised in chloroform and diphenylamine solution, and since these solutions, like the solids, are strongly coloured, it seems possible that the substances in the solid state are either polymeric modifications or solid solutions of polymolecular compounds in unimolecular. In the case of the pyridine alkyl iodides, however, which are colourless in the solid state, but coloured in various solvents, it is probable that the substances are unimolecular in the solid condition, but polymerised in certain solutions.

The view that the solids are mixtures of two forms receives support from the fact that the colour of the substance is largely dependent on the temperature. Thus, if the solids or solutions are heated, the colour is greatly intensified, whilst if cooled in liquid air the colour is greatly diminished (compare Hantzsch, *loc. cit.*).

It might be expected that heating would decompose the polymolecular modifications, since it has been shown that potassium tri-iodide is decomposed on heating (Trans., 1908, **93**, 1611).

By the addition of potassium iodide to the aqueous solutions of the methiodides, the colour is intensified. In this case the dissociation is diminished by the addition of the iodide ion, and the substance apparently polymerises.

For the sake of comparison a determination of the molecular weight of a colourless substituted ammonium iodide in diphenylamine solution was carried out.

Tetrapropylammonium iodide (a 3 per cent. solution in diphenylamine) gave M.W. = 1362 (calculated M.W = 312). Hantzsch (*loc. cit.*) also points out that dimethylammonium chloride in chloroform solution, although colourless, is strongly associated.

If the colour of the alkyl iodides of bases containing nitrogen in an aromatic ring is due to polymerisation, this colour may be due either to the production of heavy molecules, the vibration of which brings the absorption into the visible part of the spectrum, or that the extra double bonds or ring formations, produced by the polymerisation, are responsible for a vibration, which, with that due to the linking in the aromatic nucleus, produces an absorption in the visible region of the spectrum.

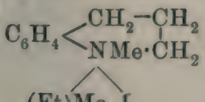
The latter theory receives support from the fact that the alkyl iodides of compounds containing nitrogen in a reduced ring are colourless. Thus piperidine and methyl iodide react with great violence when mixed together according to the following equation (Hofmann, *Ber.*, 1881, **14**, 660):

$$3C_5H_{10}NH + 3MeI \longrightarrow C_5H_{10}NMe_2I + C_5H_{10}NHMeI + C_5H_{10}NH_2I.$$

These substances are all colourless, and give colourless solutions in water and in chloroform.

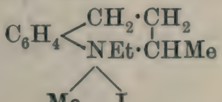
In addition, the methiodides of tetrahydroquinoline compounds are colourless.

The following compounds among others have been prepared by various investigators, and obtained colourless: Kairoline methiodide and ethiodide (I) (Wedekind, *Annalen*, 1901, **318**, 110; Claus and Stegelitz, *Ber.*, 1884, **17**, 1331). 2-Methyl-1-ethyltetrahydroquinoline methiodide (II) (Möller, *Annalen*, 1887, **242**, 321); and the substance derived from aminokairoline by the action of methyl iodide (III) (Ziegler, *Ber.*, 1888, **21**, 862).



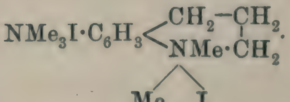
$$C_6H_4{<}\begin{matrix}CH_2-CH_2\\ NMe\cdot CH_2\end{matrix}\quad (NMe(Et)I)$$

(I.)



$$C_6H_4{<}\begin{matrix}CH_2\cdot CH_2\\ NEt\cdot CHMe\end{matrix}\quad (NEtMeI)$$

(II.)



$$NMe_3I\cdot C_6H_3{<}\begin{matrix}CH_2-CH_2\\ NMe\cdot CH_2\end{matrix}\quad (NMe_2I)$$

(III.)

Although this substance contains two iodine atoms, one is attached to nitrogen in a side-chain, and the other to nitrogen in a reduced ring; it is therefore colourless.

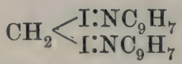
On the other hand, in the case of the alkaloids, cinchonine and quinine, which contain a piperidine and a quinoline nucleus, the monoalkyl iodides in which the iodine is attached to the piperidine nitrogen are colourless, whilst, as would be expected, the dialkyl iodides are coloured.

The action of various solvents on the hydriodides of bases was investigated as follows. Hydrogen iodide was passed into chloroform solutions of pyridine, quinoline, and *iso*quinoline. Yellow solutions were obtained, which, on shaking with water, gave colourless solutions. A similar loss of colour was noticed with an acridine solution. The hydriodides thus show the same phenomena as the alkyl iodides, and in the yellow solutions are probably polymolecular.

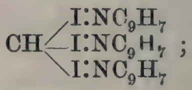
It is possible, however, that the coloured hydriodides and alkyl iodides of these cyclic ammonium bases differ in constitution from the corresponding methochlorides and colourless salts.

Quinoline combines with the various iodine derivatives of methane as follows:

One molecule of quinoline and one molecule of methyl iodide unite to produce quinoline methiodide, a yellow substance. Two molecules of quinoline unite with one molecule of methylene iodide to produce quinoline methylene iodide or methylenediquinoil hydriodide, a yellow substance (Rhoussopoulos, *Ber.*, 1883, **16**, 880). Three molecules of quinoline and one molecule of iodoform give methanetriquinoil hydriodide, which is colourless (Rhoussopoulos, *Ber.*, 1883, **16**, 202). In the two latter compounds, in addition to the structures implied by their names, it is possible that the iodine atoms are attached to the nitrogen by double bonds, thus:



$$CH_2<\begin{matrix}I{:}NC_9H_7\\ I{:}NC_9H_7\end{matrix}$$



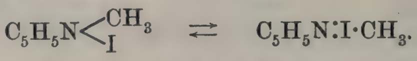
$$CH\begin{matrix}/\;I{:}NC_9H_7\\ -\;I{:}NC_9H_7\\ \backslash\;I{:}NC_9H_7\end{matrix}\;;$$

in which case the alkyl iodides might be written:

$C_5H_5N{:}I{\cdot}CH_3$ Pyridine methiodide. $C_{13}H_9N{:}I{\cdot}CH_3$ Acridine methiodide.

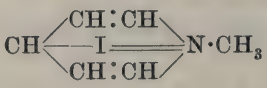
(compare Cain's ammonium chloride formula).

Or it is possible that the colour of the alkyl iodides is due to a tautomeric change between the two forms:

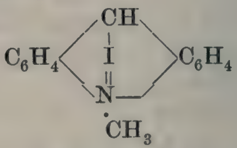


$$C_5H_5N<\begin{matrix}CH_3\\ I\end{matrix} \rightleftarrows C_5H_5N{:}I{\cdot}CH_3.$$

Other structural formulæ which might account for the colour of these iodine compounds are possible, such as



Pyridine methiodide.



Acridine methiodide.

From the results so far obtained, however, the explanation of the colour afforded by polymerisation appears the most satisfactory.

If it can be proved that the colour is due to polymerisation alone, it might be found that many other substances owe their colour to the presence of a certain amount of a polymeric modification mixed with excess of unimolecular substance. Further experiments in this connexion are in progress.

THE UNIVERSITY,
BIRMINGHAM.

CII.—*The Hydrolysis of Amygdalin by Emulsin. Part III. Synthesis of* d-*Benzaldehydecyanohydrin.*

By S. J. Manson Auld, D.Sc.(Lond.), Ph.D.

In previous communications (Trans., 1908, **93**, 1251 and 1276), it has been shown that by the action of the enzyme emulsin amygdalin is hydrolysed into dextrose, benzaldehyde, and hydrocyanic acid with intermediate formation of mandelonitrile glucoside. This glucoside, as well as amygdalin, appears to be a derivative of benzaldehydecyanohydrin, and the possible intermediate formation of this compound during the hydrolysis of amygdalin has been the subject of a considerable amount of discussion.

By the reduction of amygdalin or the mixed products of its hydrolysis by emulsin with tin and hydrochloric acid, Fileti (*Ber.*, 1879, **12**, 296) showed that phenylethylamine was produced, whereas a mixture of benzaldehyde and hydrocyanic acid gives methylamine. This may be taken as distinct proof of the presence of a benzaldehydecyanohydrin nucleus in amygdalin, but does not conclusively show its formation on hydrolysis, as the nitrile might be formed in appreciable quantities by the re-combination of the primary products of decomposition. More recently the question has again been opened by Feist (*Arch. Pharm.*, 1908, **246**, 206), who showed that the benzaldehydecyanohydrin obtained by extracting the reaction-products with ether is dextrorotatory. He consequently assumed that it is produced primarily, a synthetic product not being expected to be optically active. Investigation on this point naturally followed in this series of researches. In the meantime, it has been shown by Rosenthaler (*Arch. Pharm.*, 1908, **246**, 365; *Biochem. Zeitsch.*, 1908, **14**, 238) that an optically active benzaldehydecyanohydrin is actually produced synthetically by the action of emulsin on a mixture of benzaldehyde and hydrocyanic acid. This discovery, which has been confirmed by the author, again left the question open, as it seemed impossible to decide whether the optically active benzaldehydecyanohydrin was produced primarily, the synthetic action being ascribed to the reverse process, which would thus be capable of establishing an equilibrium, or whether it was produced secondarily, as a synthetic product, from benzaldehyde and hydrocyanic acid as the primary products of decomposition. Taking into consideration the three linkings in amygdalin which are eventually broken, namely, the "biose" ether linking, the cyanohydrin-biose ether linking, and the linking of the aldehyde-hydrocyanic acid additive compound, it would seem that the chemically feeblest is that between the hydrocyanic acid and the aldehyde, and it might reasonably be expected to be primarily broken if its combination with the hydrolysing enzyme could be assumed. From the synthetical production of benzaldehydecyanohydrin under the influence of emulsin, this combination may be taken as proved, and it is consequently suggested that the intermediate formation of the nitrile need not be taken as highly probable and merely awaiting definite proof, as has hitherto generally been done (see Feist, *loc. cit.*).

If the formation of an active mandelonitrile from amygdalin be due, partly at least, to the synthetic process, it was assumed that, like all reversible enzyme actions hitherto studied, the synthetic action would have a much lower velocity than the original decomposition. Working with comparable concentrations, it has been found, however, that the synthetic formation of *d*-benzaldehydecyanohydrin proceeds much more readily than that from amygdalin, thus making it seem probable that the formation of the nitrile in the latter case is due to a secondary reaction. That the equilibrium is not identical after a considerable lapse of time is due, no doubt, to the disturbing influence in the hydrolysis of amygdalin of the presence of undecomposed glucoside, mandelonitrile glucoside, and dextrose. The synthetic action might, however, be ascribed to a special enzyme. This would serve as an explanation of the fact that the active and racemic forms of benzaldehydecyanohydrin both appear to be hydrolysed by "emulsin," and the reaction is reversible, at least in the case of the dextro-compound, where it can readily be followed.

These facts render it highly probable that the cyanohydrin nucleus suffers complete disruption, and that the nitrile, if formed at all, exists only for a short time and to a limited extent.

Formation of d-*Benzaldehydecyanohydrin from Amygdalin.*—Quantitative observations regarding the formation of an optically active mandelonitrile from the hydrolysis of amygdalin were made in a series of experiments carried out by the method described by Feist (*loc. cit.*), special care being taken in the choice of conditions to avoid racemisation. The absolutely dry chloroform solution was brought to a volume of 10 c.c., this forming solutions containing about 5 per cent. of benzaldehyde or mandelonitrile in No. 1, and about 8 per cent. in Nos. 2 and 3; the rotations observed, although invariable, were very small. The following results are chosen from a number of experiments:

Volume of Solution = 50 c.c. Temperature = 35°.

	Weight of amygdalin, grams.	Weight of emulsin, gram.	Time of action, hours.	Rotation of 1-dcm. tube.
1.	2	0·2	2	+0°6′
2.	3	0·3	3	+0 9
3.	3	0·3	4	+0 8

These rotations are considerably smaller than those obtained by Feist, and it is significant that his higher values were obtained only after several days, whereas in the above experiments about 80 per cent. of the amygdalin had been hydrolysed after a few hours. When the reaction was allowed to proceed for a longer period, this rotation increased, although the extent of hydrolysis, as measured by the quantity of hydrocyanic acid formed, did not increase proportionally. Thus, in an experiment carried out under exactly similar conditions to No. 2 and with the same quantities of substances, a rotation of +0°14′ was obtained after the reaction had proceeded for eighteen hours.

Synthesis of d-*Benzaldehydecyanohydrin from Benzaldehyde and Hydrocyanic Acid by the Action of Emulsin.*—Preliminary experiments having confirmed Rosenthaler's statement that an appreciable formation of a dextrorotatory substance takes place when emulsin is allowed to act on a mixture of pure benzaldehyde and an aqueous solution of hydrocyanic acid, more exact measurements were made with quantities of the reacting substances exactly comparable with those obtained in the hydrolysis of amygdalin in the previous experiments. In this way, comparable rotations could be obtained denoting the extent of the principal and the reverse actions. Some of the results obtained are quoted below:

Volume of Solution = 50 c.c. Temperature = 35°.

Weight of benzaldehyde, grams.	Weight of HCN, grams.	Weight of emulsin, grams.	Time of action, hours.	Volume of chloroform solution, c.c.	Rotation in 1-dcm. tube.
2·0	0·8	1·0	3·0	35·0	+0°51′
1·0	0·4	0·5	3·5	17·5	+1 9
8·0	3·2	2·0	24·0	100·0	+0 40
10·0	4·0	2·0	24·0	100·0	+0 58

Action of Emulsin on Benzaldehydecyanohydrin.—Benzaldehydecyanohydrin was prepared by the action of hydrochloric acid on a mixture of potassium cyanide and benzaldehyde. After purification, the product was found to have a slight lævorotation.

Eleven grams of the nitrile were mixed with 50 c.c. of water and 0·5 gram of emulsin and kept at the temperature of the room for three days. The mixture was then extracted with ether, the ethereal extract dried with anhydrous sodium sulphate, and, after evaporation of the ether, redissolved in dry chloroform and made up to 100 c.c.; the rotation of this solution in a 2-dcm. tube illuminated with sodium light was +0°36′. The aqueous solution, after removing the cyanohydrin, was found by titration with silver nitrate solution to contain 0·090 gram of hydrocyanic acid. A control experiment without emulsin gave a rotation in chloroform of −0°5′, and showed the presence in the aqueous solution of 0·050 gram of hydrocyanic acid. In this case, where the cyanohydrin is primarily decomposed by emulsin prior to the synthesis of the optically active compound, the direct action proceeds more rapidly than the reverse process.

Scientific and Technical Department,
Imperial Institute, S.W.

CIII.—*Substituted Dihydrobenzenes. Part III. The So-called 1 : 1-Dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene of Harries and Antoni.*

By Arthur William Crossley and Nora Renouf.

In Part II of this work (Trans., 1908, **93**, 637), wherein the properties of 1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene and 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene were described, the opinion was expressed that the evidence then forthcoming was insufficient definitely to establish the constitution of the hydrocarbon designated 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene by Harries and Antoni (*Annalen*, 1903, **328**, 88), although showing that the hydrocarbon could not have the structure assigned to it. Further work has now been carried out with the hydrocarbon, and direct evidence is forthcoming that it is a mixture of 1 : 2-dimethyl*cyclo*hexadiene and 1 : 3-dimethyl*cyclo*hexadiene, and very probably does not contain any of the isomeride with the methyl groups attached to the same carbon atom.

The hydrocarbon was prepared according to the directions of Harries and Antoni (*loc. cit.*, p. 109), by reducing 400 grams of the dioxime of dimethyldihydroresorcin * in quantities of 5 grams at one time. The phosphate of the resulting 3 : 5-diamino-1 : 1-dimethyl*cyclo*hexane, isolated as fine white, silken needles by crystallisation from diluted alcohol, was submitted to the process of dry distillation, when 30 grams of hydrocarbon were obtained, giving numbers on analysis agreeing with those required for a dimethyl*cyclo*hexadiene:

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* The oxime was obtained in 85 per cent. of the theoretical amount by dissolving 20 grams of dimethyldihydroresorcin in absolute alcohol, adding 28 grams of dry, powdered hydroxylamine hydrochloride, 42 grams of dry, powdered potassium acetate, and allowing to stand for three days. The whole was then heated to the

0·1793 gave 0·5834 CO_2 and 0·1811 H_2O. C = 88·74; H = 11·22.

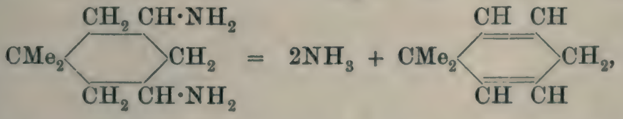
C_8H_{12} requires C = 88·88; H = 11·11 per cent.

The non-constant boiling point at once gave indications that the substance was not homogeneous; at the first distillation the largest amount boiled from 134—138°, and after repeated fractionation somewhat lower; but no portion of constant boiling point could be obtained, the hydrocarbon passing over anywhere from 126—136°.

The hydrocarbon gave marked colour reactions, which agreed closely with those given by Harries and Antoni (p. 118) for 1 : 2- and for 1 : 3-dimethyl*cyclo*hexadienes; the colour with sulphuric acid was yellowish-red, and certainly not raspberry-red.

Attempts to prepare a nitrosyl chloride from the hydrocarbon gave negative results.

Harries and Antoni believed their hydrocarbon to have the double bonds in the 2 : 5 position, that is to say, that the elimination of ammonia from the cyclic diamine had taken place in one way



only, and this despite the fact that in other cases quoted by them the elimination of ammonia took place in two ways, giving hydrocarbons isomeric by reason of the different positions of the double bonds which they contained. If their hydrocarbon had the above formula, it should readily absorb 4 atoms of bromine, whereas if the double bonds were in the 2 : 4 position (Thiele linking), it would be expected to only absorb 2 atoms of bromine. This was shown

boiling point of alcohol, filtered, washed with a little hot alcohol, the filtrate evaporated to about 100 c.c., and then diluted to 500 c.c. with water, when the oxime (m. p. after recrystallisation, 175—176°) crystallised out in flattened needles.

In the preparation of the base after steam distillation, the residue was acidified, when a little more than 100 grams of solid were obtained, soluble in potassium hydroxide, re-precipitated by acid, and crystallising from dilute formic acid in stout, transparent needles. These contained nitrogen, but had no definite melting point, and decomposed somewhat violently on heating, so that it was extremely difficult to obtain concordant results on analysis. For these reasons, the material was not further examined.

in Part II of this research to be the case with 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene and 1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene respectively.

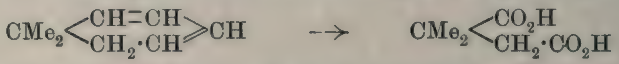
In order to test the point, a chloroform solution of bromine was added to a solution of the hydrocarbon in dry chloroform, when a pale violet colour was developed, gradually deepening, then becoming green, once again changing to deep violet, which suddenly became pale reddish-brown, and hydrogen bromide was evolved. At this point the molecular absorption was 162. Bromine was then taken up very slowly by the solution, and the absorption could only be followed by comparing the colour with that of a solution of similar tint (see Trans., 1908, **93**, 650). The absorption was finally complete after three hours, but as a considerable amount of hydrogen bromide was evolved in the latter stages, not much reliance is to be placed on the fact that the final molecular absorption was 256.

A similar result was obtained when the reaction was performed in glacial acetic acid solution, the first number being 163 and the final one 265. No solid product was obtained on evaporating either the chloroform or acetic acid solutions.

These experiments prove that the substance does not consist of a single hydrocarbon with the double bonds in the 2 : 5-position, and therefore capable of absorbing 4 atoms of bromine, but that it is mixed with an isomeride with the double bonds in the Thiele position, capable of absorbing, therefore, only 2 atoms of bromine.

Further, if the hydrocarbon were 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene, then, on treatment with a mixture of nitric and sulphuric acids, it would give the two isomeric trinitro-*o*-xylenes (Trans., 1908, **93**, 634), but it does not; for on nitrating 2 grams as described (*ibid.*, p. 646), 0·2 gram of a nitro-product was obtained, which crystallised from alcohol in glistening needles melting at 181—182°, nor was this melting point altered on mixing with pure trinitro-*m*-xylene (m. p. 182°).

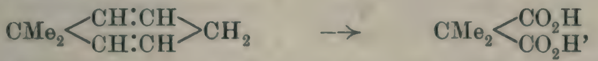
The process of oxidation is usually recognised as one of the chief aids in elucidating the structure of organic substances. Now, the present authors have oxidised with potassium permanganate many hydroaromatic hydrocarbons, alcohols, and ketones containing the *gem*-dimethyl group, and, in all cases, have succeeded in isolating a product which definitely established the presence of this grouping. Thus 1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene gives *as*-dimethylsuccinic



$$\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CH{=}CH}\\ \mathrm{CH_2\cdot CH}\end{matrix}\!\!>\!\mathrm{CH} \quad\longrightarrow\quad \mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

acid (Trans., 1908, **93**, 633), and other examples are mentioned in the following references: Trans., 1903, **83**, 110; 1905, **87**, 1488; 1906, **89**, 1556; 1907, **91**, 63.

If, therefore, the hydrocarbon of Harries and Antoni is 1 : 1-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene, it should yield on oxidation with potassium permanganate, dimethylmalonic acid (compare Trans., 1908, **93**, 651):



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH{:}CH}\\\mathrm{CH{:}CH}\end{matrix}>\mathrm{CH_2} \quad\longrightarrow\quad \mathrm{CMe_2}<\begin{matrix}\mathrm{CO_2H}\\\mathrm{CO_2H}\end{matrix},$$

but Harries and Antoni state (p. 112) that they could not with certainty prove the presence of this acid among the oxidation products of their hydrocarbon with potassium permanganate. The present authors have been equally unsuccessful, for on oxidising 9 grams of the hydrocarbon with potassium permanganate, the only definite product isolated was acetic acid, although evidence was obtained of the presence of a succinic acid and also of traces of phthalic and *iso*phthalic acids. In other words, no single piece of evidence has been obtained which directly establishes the presence of the *gem*-dimethyl group in the hydrocarbon.

When dilute nitric acid is used as an oxidising agent, the result is in some cases the breaking down of the hydrocarbon at the double bonds, as with $\Delta^{1:3}$-*cyclo*hexadiene (Trans., 1904, **85**, 1423), or the oxidation results in the production of an aromatic carboxylic acid as with cantharene, which gives *o*-toluic and phthalic acids (Piccard, *Ber.*, 1879, **12**, 579), or with 1 : 3-dimethyl*cyclo*hexadiene, which gives toluic and *iso*phthalic acids (Wallach, *Annalen*, 1890, **258**, 329).

Although in certain cases, where concentrated nitric acid or a nitrating mixture has been used, a wandering of a methyl group has been observed when both methyl groups are attached to the same carbon atom (Trans., 1908, **93**, 646), it does not appear that such wanderings have ever been brought about under the influence of dilute nitric acid; but in order to obtain some further evidence on this point, 2 grams of 1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene (Trans., 1902, **81**, 821), prepared by the action of sodium in moist ethereal solution on 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene, were oxidised with dilute nitric acid. On evaporation to dryness, 0·8 gram of solid remained, which was proved to consist of a mixture of dimethylmalonic and dimethylsuccinic acids by the method already described (Trans., 1902, **81**, 829), and no evidence was obtained of the production of an aromatic carboxylic acid. In this case, therefore, oxidation takes place at the double bonds, and a methyl group does not wander.

It appeared, therefore, that if it were possible to produce a toluic or phthalic acid from the hydrocarbon of Harries and Antoni by oxidation with diluted nitric acid, direct proof would be established that it does not contain the *gem*-dimethyl group. Moreover, it is evident from the following passage (p. 101) in the paper by Harries and Antoni that they would have accepted such evidence as showing that in the production of their hydrocarbon a methyl group had wandered: "We have considered the possibility that, as a consequence of the high temperature attained during the dry distillation of the phosphate of 3:5-diamino-1:1-dimethyl*cyclo*hexane, our dimethyl*cyclo*hexadiene has undergone a change, consisting in the wandering of a methyl group from the 1:1- to the 1:2-position. We have, however, relinquished this opinion. Piccard has shown that cantharene can be easily converted into *o*-toluic and phthalic acids by means of dilute nitric acid, but from our dimethyl*cyclo*hexadiene, under similar conditions, no *o*-toluic acid could be obtained."

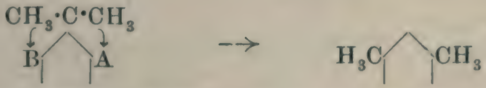
Yet the true explanation of the matter is that a methyl group does wander in the formation of the hydrocarbon, as proved by the following experiments, where, using as little as 3 grams of the hydrocarbon, appreciable quantities of ortho- and *iso*-phthalic acids have been isolated on oxidation with dilute nitric acid followed by potassium permanganate, as recommended by Wallach (*Annalen*, 1890, **258**, 329).

Three grams of the hydrocarbon were added to 30 c.c. of a mixture of one volume of fuming nitric acid and two volumes of water, when the whole gradually became hot, a reaction set in, and an oil separated. After heating six hours on the water-bath, all the oil had disappeared, and on standing overnight a white solid (0·4 gram) had separated, and a further 0·3 gram was obtained by evaporating the solution. This softened when heated in a capillary tube at 90°, began to melt at 180°, and was not completely melted until 220°, and consisted probably of a mixture of toluic and phthalic acids (compare Wallach, *ibid.*). The solid was suspended in water and oxidised with potassium permanganate by heating on the water-bath, etc. On evaporating the resulting liquid to a small bulk and acidifying, 0·2 gram of solid resulted (Filtrate = A), which was sublimed in two fractions; the first gave the fluorescein reaction and had a very indefinite melting point, shrinking at 180—200° and melting at 250—280°. It evidently consisted of a mixture of phthalic and *iso*phthalic acids. The second fraction did not give the fluorescein reaction, did not melt at 300°, and gave the following figures on analysis:

$C = 57·63$; $H = 3·85$.

$C_8H_6O_4$ requires $C = 57·83$; $H = 3·61$ per cent.

These data prove that the substance is either *iso*phthalic or terephthalic acid; but inasmuch as trinitro-*m*-xylene is obtained on nitrating the hydrocarbon, it would be *iso*phthalic acid. The filtrate A (see above) was extracted ten times with ether, the solution dried, and evaporated, when the residue (0·2 gram) solidified immediately. After crystallisation from hydrochloric acid, it melted at 183—184°, nor was this melting point altered on mixing with pure phthalic acid. Moreover, it gave a marked fluorescein reaction, an anhydride melting at 128—129°, and from this an anilic acid crystallising in glistening, transparent prisms melting at 166—167°. The melting points of the anhydride and the anilic acid were not altered on admixture with specimens of these derivatives prepared from pure phthalic acid. Obviously during dry distillation of the phosphate of 3 : 5-diamino-1 : 1-dimethyl*cyclo*hexane a methyl group must wander, partly into an ortho- and partly into a meta-position. The wanderings of methyl groups which have so far been noticed by the present authors (Trans., 1904, **85**, 264; 1906, **89**, 875; 1908, **93**, 633) have only taken place into an ortho-position, but the cases are not exactly parallel, for in the above instance the wandering concerns the passage of a saturated hydroaromatic substance into an unsaturated hydroaromatic substance, whereas in the other instances hydroaromatic substances are converted by the change into members of the aromatic series. There is, moreover, another possibility, namely, that instead of only one group wandering, both groups swing into ortho-positions, one to the carbon atom A, and the second to the carbon atom B:



The positions of the methyl groups in the resulting hydrocarbon would then be 1 : 3, and this process would not necessitate the assumption that a methyl group wanders into a meta-position.

Action of Dehydrating Agents on Methylheptenone.

Having shown that the hydrocarbon of Harries and Antoni consisted of a mixture, containing as one constituent 1 : 3-dimethyl*cyclo*hexadiene, it appeared to be desirable to compare the properties of these two hydrocarbons more closely, particularly regarding their behaviour on oxidation with potassium permanganate.

1 : 3-Dimethyl*cyclo*hexadiene is said to have been obtained pure by the action of dehydrating agents on methylheptenone, and sulphuric acid was first employed, as recommended by Verley (*Bull. Soc. chim.*, 1897, [iii], **17**, 180). One hundred and twenty grams of methylheptenone gave 48 grams of a hydrocarbon boiling not

very constantly at 130—132°, having a decided odour of xylene, and giving the following figures on analysis:

0·1223 gave 0·3960 CO_2 and 0·1304 H_2O. C = 88·30; H = 11·84.
C_8H_{12} requires C = 88·88; H = 11·11 per cent.
C_8H_{14} „ C = 87·27; H = 12·73 „

This suggested that the hydrocarbon was a mixture of dimethyl*cyclo*hexadiene and dimethyl*cyclo*hexene, which would not be altogether surprising, as in such reactions sulphuric acid has been shown to act as a reducing agent (Wagner, *Ber.*, 1894, **27**, 1638). Zinc chloride was next used as recommended by Wallach (*Annalen*, 1890, **258**, 326), but again analysis showed the resulting hydrocarbon (b. p. 131—133°) to be a mixture:

0·1110 gave 0·3600 CO_2 and 0·1162 H_2O. C = 88·45; H = 11·64.

Finally phosphoric oxide was employed, without, however, producing any appreciable difference in the composition of the hydrocarbon (b. p. 130—133°), as is seen from the following figures:

0·1163 gave 0·3764 CO_2 and 0·1223 H_2O. C = 88·26; H = 11·68.

On communicating these results to Professor Wallach, he replied that the hydrocarbon obtained by the dehydration of methylheptenone is not homogeneous (compare Wallach, *Terpene und Campher*, p. 351). During the reaction considerable quantities of *m*-xylene are produced, but no hydrogen is liberated, and it is probably used up in reducing the dimethyl*cyclo*hexadiene to dimethyl*cyclo*hexene. We wish to thank Professor Wallach for his courtesy in supplying us with this information and for allowing us to make this statement. As Professor Wallach is at present working out this problem, we have no intention of continuing on the same lines, and simply place on record a few results of our incompleted experiments.

Oxidation of the Hydrocarbon with Potassium Permanganate in Aqueous Solution.—Seventeen grams of the hydrocarbon were oxidised at atmospheric temperature with a 4 per cent. solution of potassium permanganate solution. The reaction proceeded very slowly, and was not completed until thirty-four hours, facts which are alone sufficient to show that the substance contained something less readily oxidised than a dimethyl*cyclo*hexadiene. On completion of the reaction the liquid had a decided odour of xylene, and it was therefore distilled in a current of steam, when, after separating and drying the liquid lighter than water, 2 grams of *m*-xylene were obtained. This was proved by the facts that it did not decolorise a solution of bromine in chloroform, it boiled at 136—139°, and on treatment with a nitrating mixture gave an almost theoretical yield of pure trinitro-*m*-xylene melting at 182°.

After working up the residue of the steam distillation in the ordinary way, there was obtained 0·7 gram of a solid, which sublimed in colourless, fern-like aggregates of needles. These did not melt at 300°, and on treatment with phosphorus pentachloride, and then pouring into methyl alcohol, gave sheaves of fine silken needles melting at 64—65° (methyl *iso*phthalate, m. p. 64—65°), thus proving that the original solid consisted of *iso*phthalic acid. On steam-distilling the liquid from which the *iso*phthalic acid had separated, 2·7 grams of a volatile fatty acid were obtained, probably acetic acid, and the residue of the distillation yielded, on extraction with ether, 3 grams of an oil, which contained a ketonic acid.

Oxidation of the Hydrocarbon with Potassium Permanganate in Acetone Solution.—Fifteen grams of the hydrocarbon were suspended in a mixture of 500 c.c. acetone and 100 c.c. of water, and powdered potassium permanganate gradually added. The whole was filtered from manganese dioxide, distilled in a current of steam, and after evaporation to a small bulk, extracted ten times with ether (extracted liquid = B), the ethereal solution dried over potassium carbonate, and the ether evaporated, when the residue solidified at once (1·8 grams). It was purified by fractional extraction and crystallisation from light petroleum (b. p. 40—60°), when there was obtained a solid crystallising in transparent, silken needles, melting at 90°:

0·1029 gave 0·2511 CO_2 and 0·1024 H_2O. C = 66·55; H = 11·05.
$C_8H_{16}O_2$ requires C = 66·66; H = 11·11 per cent.

This substance sublimes in transparent needles, does not absorb bromine, and does not give a colour with concentrated sulphuric acid. It is evidently the crystalline glycol mentioned by Wallach (*Terpene und Campher*, p. 351), and is probably also the indifferent crystalline substance mentioned by Harries and Antoni (p. 114), who prepared the so-called 1 : 3-dimethyl*cyclo*hexadiene from methylheptenone, without, however, observing it to be a mixture.

There is produced, in addition to this substance, a second neutral compound, which has a lower melting point, but has not been further investigated.

The liquid B (see above) was acidified and extracted with ether, when 1 gram of an oil was obtained, which contained a ketonic or ketonic acids, because it gave the iodoform reaction, and also a semicarbazone or mixture of semicarbazones, crystallising from dilute alcohol and melting at 129—131°, but not becoming clear until 182°, when gas was evolved.

It would appear, therefore, that the hydrocarbon prepared by the dehydration of methylheptenone contains considerable quantities of *m*-xylene and dimethyl*cyclo*hexene, and probably not more than 30 to 40 per cent. of dimethyl*cyclo*hexadiene.

In comparing the properties of this hydrocarbon with a dimethyl*cyclo*hexadiene prepared by Harries and Atkinson (*Ber.*, 1902, **35**, 1175), Harries and Antoni say that the former is more easily converted into trinitro-*m*-xylene than the latter. This is not surprising considering that, as now shown, the former contains considerable quantities of *m*-xylene.

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CIV.—*Affinity Constants of Hydroxy- and Alkyloxy-Acids.*

By Alexander Findlay, William Ernest Stephen Turner, and Gertrude Emily Owen.

In connexion with investigations of the influence of the hydroxy- and alkyloxy-groups on the velocity of saponification (Findlay and Turner, Trans., 1905, **87**, 747), of which it is hoped soon to publish a further account, it became necessary to determine the affinity constants of several of the acids used in the preparation of the esters investigated. The acids which have thus been examined are phenylmethoxyacetic acid, phenylethoxyacetic acid, phenylpropoxyacetic acid, α-hydroxy-β-phenylpropionic acid, and β-hydroxy-β-phenylpropionic acid. The measurements were carried out in the usual manner with induction coil and telephone; and in calculating the conductivity of the acid, that of the water was not subtracted.

1. *Phenylmethoxyacetic Acid.*

The acid was prepared by acting on methyl phenylchloroacetate with sodium methoxide in methyl-alcoholic solution (Meyer and Boner, *Annalen*, 1883, **220**, 45). The small amount of chloro-ester which escaped conversion was converted into sodium mandelate by the action of sodium hydroxide, and could thus be separated by crystallisation from the sodium salt of phenylmethoxyacetic acid. The free acid was isolated by decomposing the sodium salt with sulphuric acid, and was purified by repeated recrystallisation from benzene and light petroleum. The values obtained for the conductivity and affinity constant are as follows:

v.	Λ.	$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.	100 k.
32	53·88	0·143	0·0748
64	73·50	0·195	0·0742
128	98·95	0·263	0·0734
256	130·6	0·347	0·0722
512	168·5	0·448	0·0710
1024	211·1	0·561	0·0702

Λ_∞ (calc.) = 376. Conductivity of water = $1·7 \times 10^{-6}$ mhos.

Another series of determinations gave values ranging from 0·0732 to 0·0706. Conductivity of water = $1·5 \times 10^{-6}$ mhos.

As is seen from the above table, the values of the constant continuously decreases with increase in dilution, so that one cannot take the mean as the most probable value. This decrease in the value of the affinity constant is by no means of rare occurrence (see, for example, Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 174), and may be attributed to various causes, of which perhaps the most common is oxidation, or other chemical change, which may be accelerated by the platinum-black on the electrodes. In such cases it is therefore better to take as the value of the affinity constant that which is obtained with fresh solutions. We may therefore take as the best value of the affinity constant the mean of 0·0732 and 0·0748, namely, 100 k = 0·074.

The affinity constant of the active *l*-phenylmethoxyacetic acid was determined by W. Roth (Trans., 1899, **75**, 767), who at two dilutions found the values 0·0709 and 0·0748.

2. *Phenylethoxyacetic Acid.*

This acid was prepared by decomposing the sodium salt (Findlay and Turner, Trans., 1905, **87**, 755) with sulphuric acid, whereby the phenylethoxyacetic acid was obtained as a viscid, pale yellow oil, which could not be made to crystallise. It was well washed with water to remove any mandelic acid which might be present, and was then dissolved in ether and the solution dried over fused sodium sulphate. An analysis of the silver salt gave Ag = 37·39 per cent., whereas theory requires 37·35 per cent.

For the determination of the affinity constant of the acid, the oil was stirred with carbon dioxide-free water at 25° in a closed vessel until the solution was saturated, as indicated by its conductivity remaining constant. The concentration of the solution was then determined by titration with standard alkali. Later, the acid was purified by distillation under diminished pressure; but the numbers obtained did not greatly differ from those obtained by the washing-out method just described. The acid, we believe, may be regarded as pure. The values obtained for the conductivity are as follows:

v.	Λ.	$\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$.	100 k.
22·28	38·38	0·102	0·0523
44·56	53·59	0·143	0·0534
89·12	73·10	0·195	0·0530
178·24	97·88	0·261	0·0517
356·48	128·0	0·341	0·0497
712·96	163·2	0·435	0·0467

Λ_∞ (calc.) = 375. Conductivity of water = $2{\cdot}1 \times 10^{-6}$ mhos.

Another series gave values varying from 0·0539 to 0·0482. As in the case of the methoxy-acid, we have taken as the most probable value of the affinity constant the mean of the initial values in the two series, namely, 100 k = 0·053.

3. *Phenylpropoxyacetic Acid.*

The acid was prepared by decomposing the sodium salt with sulphuric acid (Findlay and Turner, Trans., 1905, **87**, 756). It was obtained as a sparingly soluble, pale yellow oil. It was well washed with water to free it from mandelic acid, and was purified by distillation under diminished pressure. The following values were obtained for the conductivity:

v.	Λ.	$\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$.	100 k.
27·11	40·57	0·109	0·0490
54·22	56·59	0·153	0·0497
108·44	76·87	0·205	0·0488
216·88	102·4	0·275	0·0481
433·76	134·0	0·358	0·0461
867·52	170·0	0·455	0·0437

Λ_∞ (calc.) = 374. Conductivity of water = $2{\cdot}1 \times 10^{-6}$ mhos.

Another determination gave values varying from 0·0494 to 0·0455. As the value of the affinity constant of this acid, therefore, we have taken 100 k = 0·049.

4. *α-Hydroxy-β-phenylpropionic Acid.*

The acid was prepared by Conrad's method (*Annalen*, 1881, **209**, 241). It was purified by crystallisation. The following are the values of the conductivity:

v.	Λ.	$\alpha = \dfrac{\Lambda_v}{\Lambda_\infty}$.	100 k.
109	51·04	0·136	0·0196
218	68·43	0·182	0·0186
436	92·4	0·246	0·0184
		Mean =	0·0188

Λ_∞ (calc.) = 376. Conductivity of water = $2{\cdot}4 \times 10^{-6}$ mhos.

As the mean of five other determinations we obtained the value of 100 $k = 0·0188$. As the value of the affinity constant we may therefore take 100 $k = 0·019$.

5. *β-Hydroxy-β-phenylpropionic Acid.*

This acid was prepared by Fittig and Binder's method (*Annalen*, 1879, **195**, 131), by acting on cinnamic acid with hydrobromic acid, and treating the phenylbromopropionic acid with boiling water. The acid was purified by recrystallisation. The following are the values of the conductivity:

v.	Λ.	$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$.	100 k.
109	23·86	0·0635	0·00394
218	33·47	0·0890	0·00399
436	46·25	0·123	0 00396
872	65·42	0·174	0·00420
		Mean =	0·00396

Λ_∞ (calc.) = 376. Conductivity of water = $2·4 \times 10^{-6}$ mhos.

Other three series of determinations gave as mean value 0·00398. As the value of the affinity constant we may take 100 $k = 0·0040$.

Relationships between the Acids.

On comparing the affinity constants of the three alkyloxy-acids with that of mandelic acid, we see that the affinity constant is in all three cases increased by the substitution of the hydrogen in the hydroxyl group by alkyl, although the increase becomes less with increase in the molecular weight of the alkyl group. The ratios of the affinity constants of the alkyloxy-acids to that of mandelic acid are 1·77, 1·27, and 1·17 respectively. Such an increase in the value of the affinity constant by the substitution of a hydroxy- by an alkyloxy-group was also found by Ostwald (*loc. cit.*) in the case of glycollic acid and its methyl and ethyl derivatives. In these cases the affinity constants of the methyl and ethyl glycollic acids were found to be 2·2 and 1·54 times as great as that of glycollic acid itself.

On comparing the affinity constant of α-hydroxy-β-phenylpropionic acid with that of phenylpropionic acid, we find that the former is 8·2 times as great, while the ratio of the affinity constant of β-hydroxy-β-phenylpropionic acid to that of phenylpropionic acid is 1·74. These numbers are rather lower than the factors given by Wegscheider (*Monatsh.*, 1902, **23**, 289) for the influence of the hydroxy-group in the α- and β-position respectively, namely, 8·4 and 2·31.

The influence of the phenyl group in the β-position is obtained from a comparison of the affinity constant of α-hydroxy-β-phenylpropionic acid with that of lactic acid, or of the affinity constant of β-hydroxy-β-phenylpropionic acid with that of β-hydroxypropionic acid. The factors obtained in this way are 1·36 and 1·27 respectively. This is considerably less than the influence of the phenyl group in the α-position, which, from a comparison of phenylacetic acid with acetic acid, or of mandelic acid with glycollic acid, is found to be 3·1 and 2·8 respectively.

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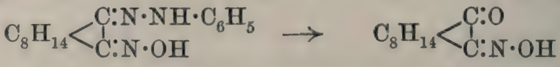
CV.—*Studies in the Camphane Series. Part XXVI. Aryl Derivatives of Iminocamphor.*

By MARTIN ONSLOW FORSTER and TOM THORNLEY.

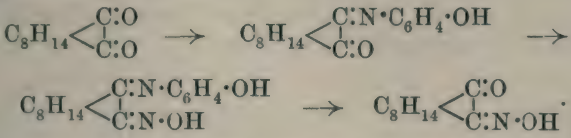
FROM time to time during the past five years attempts have been made by one of us to prepare that monoxime of camphorquinone which, owing to the asymmetry of the camphor molecule, would be structurally distinct from the two known stereoisomeric forms of *iso*nitrosocamphor. The line of attack has been based on the theoretical possibility of oximating a selected α-derivative of camphor and afterwards replacing the α-substituent by oxygen without disturbing the oximino-group. These experiments have resulted in unbroken failure. When they escaped the well-known difficulty which attends the preparation of oximes from α-derivatives of camphor, they have been checked at the second stage, and the present communication adds another to the list; the oxime of camphorquinonephenylhydrazone was prepared in the hope that by the action of benzaldehyde or of acids the transformation



$$C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}N\cdot OH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C{:}O\\ |\\ C{:}N\cdot OH\end{matrix}$$

might be brought about, but the plan in question has not materialised.

The observation that camphorquinone readily undergoes condensation with *p*-aminophenol, however, suggested a new class of derivatives which might lend themselves to the purpose indicated above, and the action of hydroxylamine on the resulting *p*-hydroxyphenyliminocamphor was therefore studied with the object of completing the following series :

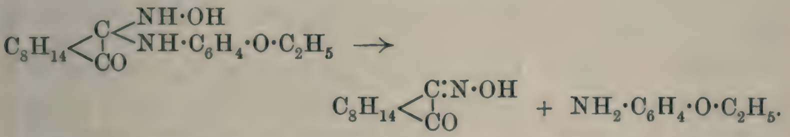


$$C_8H_{14}<\begin{array}{l}C{:}O\\ |\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_4\cdot OH\\ |\\ C{:}O\end{array} \longrightarrow$$

$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_4\cdot OH\\ |\\ C{:}N\cdot OH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}O\\ |\\ C{:}N\cdot OH\end{array}.$$

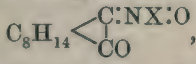
Again the scheme proved fruitless, but as the reason for this failure came to light, and gives experimental probability to the commonly accepted explanation of oxime production, it seems worth recording.

When hydroxylamine acts on *p*-hydroxyphenyliminocamphor, the the only products are *p*-aminophenol and *iso*nitrosocamphor, just as the last-named substance is regenerated from its *N*-methyl ether (Trans., 1904, **85**, 898). Proceeding in the same way with *p*-ethoxyphenyliminocamphor, however, there has been isolated an intermediate hydroxylamino-derivative, which, although quite stable in the dry state, is quickly resolved into *p*-phenetidine and *iso*nitrosocamphor by the action of organic solvents or of alkalis :



$$C_8H_{14}<\begin{array}{l}C<\begin{array}{l}NH\cdot OH\\ NH\cdot C_6H_4\cdot O\cdot C_2H_5\end{array}\\ |\\ CO\end{array} \longrightarrow$$

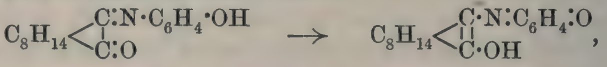
$$C_8H_{14}<\begin{array}{l}C{:}N\cdot OH\\ |\\ CO\end{array} + NH_2\cdot C_6H_4\cdot O\cdot C_2H_5.$$

Hence the failure to oximate iminocamphor and its aryl derivatives must be ascribed to the attack by hydroxylamine upon the azethenoid linking in preference to the carbonyl group, and incidentally offers fresh evidence to justify representing the *N*-alkyl ethers of *iso*nitrosocamphor by the expression  $C_8H_{14}<\begin{array}{l}C{:}NX{:}O\\ |\\ CO\end{array}$, already advocated on other grounds (Trans., 1908, **93**, 244).

Our principal reason for describing these experiments, however, follows from a polarimetric examination of the aryliminocamphors, which has showed them to be endowed with specific rotatory power of a very high order. *p*-Hydroxyphenyliminocamphor, indeed, has in pyridine the specific rotatory power $[\alpha]_D$ 1650°, corresponding with $[M]_D$ 4240°, values which we believe are unrivalled in the history of asymmetric compounds ; so far as we have been able to ascertain, the most active substances hitherto described are the *p*-santoninimide of Francesconi (*Atti. R. Accad. Lincei*, 1903, [v], **12**, ii, 204), with $[\alpha]_D$ 1135°, $[M]_D$ 2780°, and the camphoryl-ψ-semicarbazone of *p*-benzoquinone (Forster and Fierz, Trans., 1905, **87**, 722), with $[\alpha]_D$ $-1051°$ and $[M]_D$ $-3310°$. As noticed in the case of the last-named substance, the rotation of *p*-hydroxyphenyliminocamphor exhibits considerable variation with the medium in which it is examined, but the sparing solubility of the compound has precluded a wide selection of organic liquids from being made, and has necessitated the employment of highly diluted solutions.

Solvent.	Weight in 100 c.c.	Rotation in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
Pyridine............	0·4152	13°42′	1650°	4240°
Ether	0·0419	1 15	1492	3834
Ethyl acetate......	0·0956	2 42	1412	3629
Acetone	0·1810	5 5	1404	3608
Alcohol	0·0832	2 17	1372	3524
Chloroform	0·2312	6 18	1363	3503

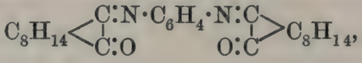
It appeared significant that whilst the previously highest recorded molecular rotation is associated with a quinonoid derivative, transformation into a substance of that class is theoretically possible in the case of *p*-hydroxyphenyliminocamphor,



$$C_8H_{14}\Big<\begin{array}{l}C{:}N\cdot C_6H_4\cdot OH\\ |\\ C{:}O\end{array} \longrightarrow C_8H_{14}\Big<\begin{array}{l}C\cdot N{:}C_6H_4{:}O\\ \|\\ C\cdot OH\end{array},$$

but having found that the methyl and ethyl ethers possess rotatory power of the same order, we conclude that the above-suggested rearrangement has not occurred to any great extent.

Besides *p*-aminophenol, *p*-anisidine, and *p*-phenetidine, we have condensed aniline, *p*-chloroaniline, and *m*-aminophenol with camphorquinone, but an experiment with *p*-nitroaniline was unsuccessful. It then became interesting to prepare *p*-phenylenebisiminocamphor,

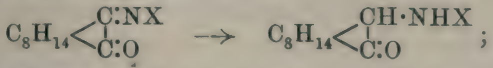


$$C_8H_{14}\Big<\begin{array}{l}C{:}N\cdot C_6H_4\cdot N{:}C\\ |\qquad\qquad\qquad\quad |\\ C{:}O\qquad\qquad\quad O{:}C\end{array}\Big>C_8H_{14},$$

for comparison with phenyliminocamphor; the substance was found to have specific rotatory power more than double that of the simpler molecule, the molecular rotation in chloroform exceeding 6000°, and reaching $[M]_D$ 6173° in pyridine. The following data as to the aryl derivatives of iminocamphor may be regarded as comparable, having been collected from solutions in chloroform.

	Weight in 100 c.c.	Rotation in 2-dcm. tube.	$[\alpha]_D$.	$[M]_D$.
p-Phenylenebisiminocamphor.........	0·6240	18°50′	1509°	6096°
p-Hydroxyphenyliminocamphor ...	0·2312	6 18	1363	3503
p-Ethoxyphenyliminocamphor	0·4312	10 47	1250	3563
p-Methoxyphenyliminocamphor ...	0·3884	9 30	1223	3314
Phenyliminocamphor	0·5050	7 20	726	1750
p-Chlorophenyliminocamphor	0·4152	5 20	642	1768
m-Hydroxyphenyliminocamphor ...	0·4124	5 12	630	1619

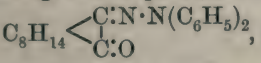
The interesting aspect of these compounds lies in the emphasis they give to the point so frequently made by workers in this field, namely, the influence exerted by unsaturated groups on specific rotatory power. Some among the aryliminocamphors readily take up two atoms of hydrogen at the azethenoid linking, and pass thereon into aryl derivatives of aminocamphor,

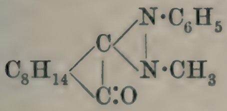


$$C_8H_{14}<\begin{matrix}C{:}NX\\ |\\ C{:}O\end{matrix} \;\longrightarrow\; C_8H_{14}<\begin{matrix}CH\cdot NHX\\ |\\ C{:}O\end{matrix}\;;$$

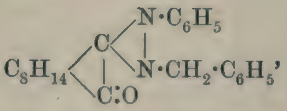
the consequent depression in molecular rotation is phenomenal, as indicated by the following measurements in chloroform.

Bases compared.	$[\alpha]_D$.	$[M]_D$.	Difference of $[M]_D$.
p-Hydroxyphenyliminocamphor.........	1363°	3503°	—
p-Hydroxyphenylaminocamphor	83	215	3288
p-Methoxyphenyliminocamphor	1223	3314	—
p-Methoxyphenylaminocamphor	68	186	3128
Phenyliminocamphor	726	1750	—
Phenylaminocamphor	127	309	1441
p-Chlorophenyliminocamphor............	642	1768	—
p-Chlorophenylaminocamphor............	94	261	1507

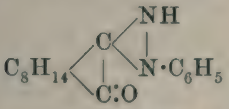
Before discussing the conclusions which these observations suggest as to the relation between structure and optical activity, it is worth while to point out that the results have a distinct bearing on the constitution of condensation products obtainable from camphorquinone and derivatives of phenylhydrazine. This matter was discussed in detail by Armstrong and Robertson (Trans., 1905, **87**, 1272), who, while ascribing to camphorquinonediphenylhydrazone the azethenoid structure,  $C_8H_{14}<\begin{matrix}C{:}N\cdot N(C_6H_5)_2\\ |\\ C{:}O\end{matrix}$, regarded the phenylmethylhydrazone and the phenylbenzylhydrazone as "phanes,"



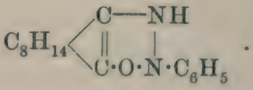
and



and represented the unsubstituted phenylhydrazone, which is tautomeric, by the two expressions:

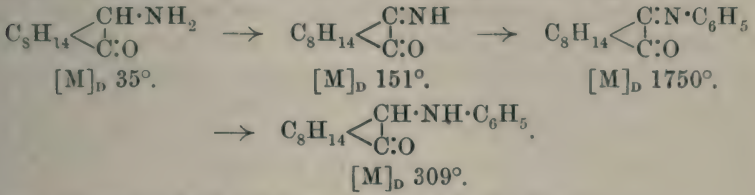


and



The arguments which led one of us to throw doubt on the propriety of regarding the phenylmethylhydrazone and phenylbenzylhydrazone as differing in structure from the diphenylhydrazone and one form of the phenylhydrazone itself have been stated at length (Trans., 1906, **89**, 222), and need not be recapitulated, although it might be mentioned in passing that one of these, which went to show that symmetry of displacement probably helps to account for the low rotation of camphorquinonediphenylhydrazone, has since been confirmed by the production of diphenylmethylenecamphor; this compound (Haller and Bauer, *Compt. rend.*, 1906, **142**, 971) stands in the same relation to benzylidenecamphor and methylenecamphor as that subsisting between dimethylbornylamine, methylbornylamine, and bornylamine, and the effect produced on rotatory power in the two series by substitution of parallel order is exactly similar, the rotation of diphenylmethylenecamphor, both specific and molecular, being lower than that of benzylidenecamphor. In the absence of fresh chemical evidence, the material brought forward in this communication must, in our opinion, finally dispose of the "phane" representation as applied to the phenylhydrazones of camphorquinone. Recalling the one argument on which that representation was based, namely, the abnormally high rotation of the unsymmetrical hydrazones, and considering that its adoption involved the transference, quite unsupported experimentally, of a methyl or a phenyl group from one atom of nitrogen to the other, it is pertinent to inquire how the advocates of the "phane" would represent the condensation products of camphorquinone with aniline derivatives. Here are substances with only two "phanogenetic" atoms, and no second substituent to transfer itself from one atom to the other; nevertheless, their rotation exceeds in some cases even the high values recorded for the phenylbenzylhydrazone and the phenylmethylhydrazone, whilst other members of the group are considerably less active.

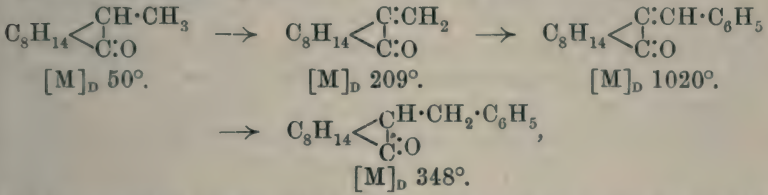
Turning now to the more general question of the relation between structure and optical activity, there is no small temptation to draw from these and other derivatives of camphor conclusions which might be expected to have still wider application. Nevertheless, we deem it advisable to proceed cautiously in this direction, principally because, in addition to the perplexing variety of factors at work, a disturbing doubt as to whether, after all, chemists have arrived at an absolute method of measuring and correlating that esoteric property known as optical activity must have enforced itself on the attention of all who have studied the problem. The stream of optically active substances poured into the literature each year has not carried our perception of the relation between unsaturation and optical activity beyond the generalisations of Tschugaeff (*Ber.*, 1898, **31**, 1775), Haller and Müller (*Compt. rend.*, 1899, **129**, 1006), Rupe (*Annalen*, 1903, **327**, 157), and Haller (*Compt. rend.*, 1903, **136**, 1222). Among these we regard the parallel drawn between the chromophoric and gyrophoric effects of various groups (Rupe and Frisell, *Ber.*, 1905, **38**, 106) one of the most illuminating, although analogy with auxochromes would have been more strict. We can only claim to furnish a few new illustrations of this principle, and the following comparison brings out (1) the small effect produced by a conjugated linking when acting alone, (2) the greatly enhanced effect of such a linking when cooperating with a benzene ring, (3) the depression due to saturating one of the units of the conjugated linking, and (4) the effect due to the phenyl group independently of the conjugated linking:



$$C_8H_{14}<\begin{array}{l}CH\cdot NH_2\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}NH\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot C_6H_5\\ |\\ C{:}O\end{array}.$$

$[M]_D$ 35°. $[M]_D$ 151°. $[M]_D$ 1750°. $[M]_D$ 309°.

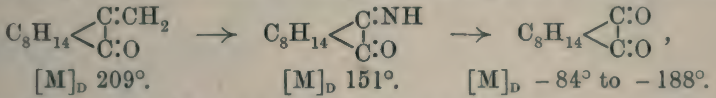
An exactly parallel gradation is shown by the following:



$$C_8H_{14}<\begin{array}{l}CH\cdot CH_3\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}CH_2\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}CH\cdot C_6H_5\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH\cdot CH_2\cdot C_6H_5\\ |\\ C{:}O\end{array},$$

$[M]_D$ 50°. $[M]_D$ 209°. $[M]_D$ 1020°. $[M]_D$ 348°.

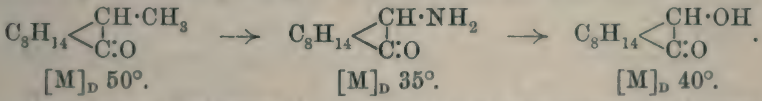
and the numerical differences between the respective members of the two series must be ascribed to the different auxorotatory effect of the carbon-nitrogen and the carbon-carbon linkings. That such differences are due to a qualitative peculiarity of the linkings in question, and do not arise solely from alterations in mass, was to be expected from the series:



$$C_8H_{14}<\begin{array}{l}C{:}CH_2\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}NH\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}O\\ |\\ C{:}O\end{array},$$

$[M]_D$ 209°. $[M]_D$ 151°. $[M]_D$ $-84°$ to $-188°$.

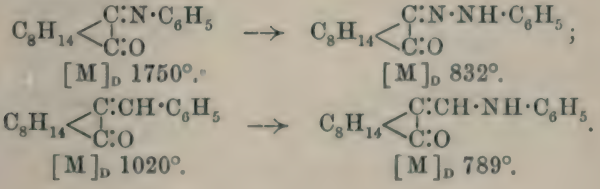
where the mass is changed by one unit only at each step; it must not be forgotten, however, that the abnormal rotation of camphorquinone may be due to some association between the oxygen atoms, the following relationship being of a more conventional character:



$$C_8H_{14}<\begin{array}{l}CH\cdot CH_3\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH\cdot NH_2\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH\cdot OH\\ |\\ C{:}O\end{array}.$$

$[M]_D$ 50°. $[M]_D$ 35°. $[M]_D$ 40°.

According to Tschugaeff (*loc. cit.*, 1781), an inactive complex (phenyl) exerts greater influence in proximity to the asymmetric system than when remote from it, and this principle can be illustrated by comparing camphorquinonephenylhydrazone and anilinomethylenecamphor (Pope and Read, this vol., 177) with phenyliminocamphor and benzylidenecamphor respectively:



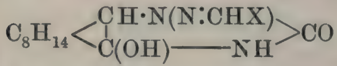
$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}O\end{array};$$

$[M]_D$ 1750°. $[M]_D$ 832°.

$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot C_6H_5\\ |\\ C{:}O\end{array} \rightarrow C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_5\\ |\\ C{:}O\end{array}.$$

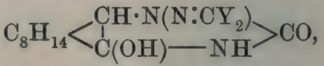
$[M]_D$ 1020°. $[M]_D$ 789°.

In each of these cases the benzene ring is divorced from the conjugated linking by an imino-group, and the result is in accordance with Tschugaeff's generalisation, although this detachment may itself be an operating factor in the depression of activity, for mere banishment from the neighbourhood of an asymmetric system will not always control the exaltatory effect of the unsaturated complex, as witnessed by the series of camphoryl-ψ-semicarbazones (Trans., 1905, **87**, 722); this comprises derivatives of the general formulæ:



$$C_8H_{14}<\begin{matrix}CH\cdot N(N:CHX)\\ |\\ C(OH)\text{———}NH\end{matrix}>CO$$

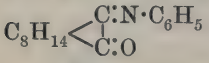
and



$$C_8H_{14}<\begin{matrix}CH\cdot N(N:CY_2)\\ |\\ C(OH)\text{——}NH\end{matrix}>CO,$$

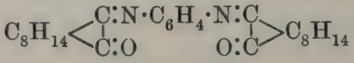
having molecular rotation varying between 300° and 2000°, whilst in the case of *p*-benzoquinonecamphoryl-ψ-semicarbazone, $[M]_D$ −3310° is attained.

Perhaps the most remarkable illustration of the principle laid down by Haller and Müller (*loc. cit.*), namely, that exaltation of optical activity is occasioned by an unsaturated linking associated with a benzene ring (compare also Rupe, *loc. cit.*, 167), is to be found by juxtaposing the following three compounds:



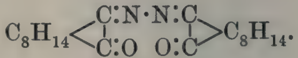
$$C_8H_{14}<\begin{matrix}C:N\cdot C_6H_5\\ |\\ C:O\end{matrix}$$

$[M]_D$ 1750°.



$$C_8H_{14}<\begin{matrix}C:N\cdot C_6H_4\cdot N:C\\ |\qquad\qquad\qquad |\\ C:O\qquad\qquad O:C\end{matrix}>C_8H_{14}$$

$[M]_D$ 6100°.

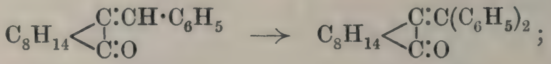


$$C_8H_{14}<\begin{matrix}C:N\cdot N:C\\ |\qquad\quad |\\ C:O\quad O:C\end{matrix}>C_8H_{14}.$$

$[M]_D$ 790°.

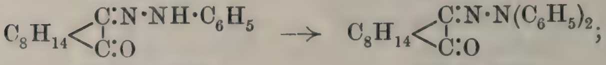
The molecular rotation of azocamphanone is modest beside that of phenyliminocamphor, although it contains four asymmetric carbon atoms and two continuous conjugated linkings; it is trifling beside that of phenylenebisiminocamphor, in which the effect of a benzene ring is superadded.

It is noteworthy that, although a benzene ring is capable of exalting specific rotatory power when attached to an ethenoid or azethenoid linking, it nevertheless happens that introducing a second phenyl group has a depressing effect on the operation of the first, provided that the two groups are attached to the same atom; the parallel with dimethylbornylamine suggests that it is the resulting symmetrical disposition which determines the effect:



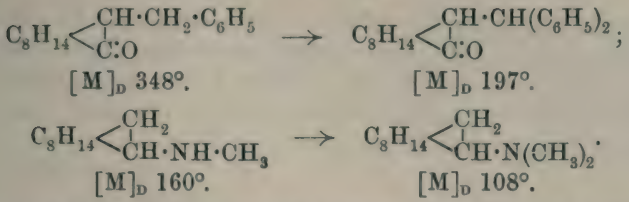
$$C_8H_{14}<\begin{matrix}C:CH\cdot C_6H_5\\ |\\ C:O\end{matrix}\quad\longrightarrow\quad C_8H_{14}<\begin{matrix}C:C(C_6H_5)_2\\ |\\ C:O\end{matrix};$$

$[M]_D$ 1020°. $[M]_D$ 907°.



$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_5\\ |\\ C:O\end{matrix}\quad\longrightarrow\quad C_8H_{14}<\begin{matrix}C:N\cdot N(C_6H_5)_2\\ |\\ C:O\end{matrix};$$

$[M]_D$ 850°. $[M]_D$ 420°.



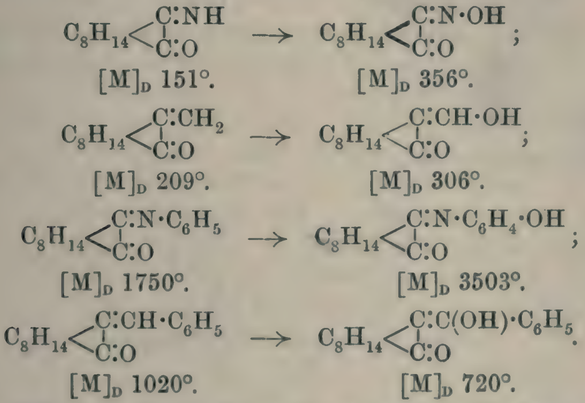
$$C_8H_{14}<\begin{array}{l}CH\cdot CH_2\cdot C_6H_5\\ \mid\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH\cdot CH(C_6H_5)_2\\ \mid\\ C{:}O\end{array};$$

$[M]_D$ 348°. $[M]_D$ 197°.

$$C_8H_{14}<\begin{array}{l}CH_2\\ \mid\\ CH\cdot NH\cdot CH_3\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH_2\\ \mid\\ CH\cdot N(CH_3)_2\end{array}.$$

$[M]_D$ 160°. $[M]_D$ 108°.

In putting forward these comparisons we recognise that, dealing as they do with camphane derivatives only, important modifications would most likely become necessary before applying them to problems in another group. The necessity for cautious procedure may be emphasised by the following illustration of contradictory effects produced by the hydroxyl group; in the first three cases, replacement of hydrogen by hydroxyl has increased the molecular rotation by 50—135 per cent., whilst the fourth comparison reveals a diminution of 30 per cent.



$$C_8H_{14}<\begin{array}{l}C{:}NH\\ \mid\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot OH\\ \mid\\ C{:}O\end{array};$$

$[M]_D$ 151°. $[M]_D$ 356°.

$$C_8H_{14}<\begin{array}{l}C{:}CH_2\\ \mid\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}CH\cdot OH\\ \mid\\ C{:}O\end{array};$$

$[M]_D$ 209°. $[M]_D$ 306°.

$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ \mid\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_4\cdot OH\\ \mid\\ C{:}O\end{array};$$

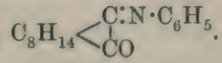
$[M]_D$ 1750°. $[M]_D$ 3503°.

$$C_8H_{14}<\begin{array}{l}C{:}CH\cdot C_6H_5\\ \mid\\ C{:}O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C{:}C(OH)\cdot C_6H_5\\ \mid\\ C{:}O\end{array}.$$

$[M]_D$ 1020°. $[M]_D$ 720°.

It is intended to continue the study of these derivatives of iminocamphor, and to compare them with analogous compounds.

EXPERIMENTAL.



Phenyliminocamphor, $C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_5\\ \mid\\ CO\end{array}$.

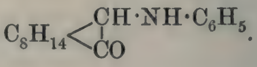
Camphorquinone and aniline in molecular proportion were heated with anhydrous sodium sulphate during several hours at 90—100°, when the product became hard on cooling; the crushed material was extracted with alcohol, from which phenyliminocamphor separated on dilution with water. Recrystallisation from hot petroleum gave long, lustrous, sulphur-yellow needles melting at 109°:

0·1994 gave 10·4 c.c. N_2 at 21° and 759 mm. N = 5·94.

$C_{16}H_{19}ON$ requires N = 5·81 per cent.

The substance is readily soluble in cold organic media and in hot petroleum. In its behaviour towards hydrochloric acid it resembles iminocamphor, dissolution being followed almost immediately by hydrolysis, this being completed on warming the liquid, from which camphorquinone is then precipitated.

Phenylaminocamphor,



$C_8H_{14}\Big<\begin{array}{l}CH\cdot NH\cdot C_6H_5\\ |\\ CO\end{array}.$

Phenyliminocamphor dissolved in ether was shaken with zinc dust and 10 per cent. potassium hydroxide until the colour was destroyed; the colourless, crystalline residue left by the ether was recrystallised three times from alcohol, forming lustrous, flat, transparent prisms melting at 80°:

0·1530 gave 0·4452 CO_2 and 0·1190 H_2O. C = 79·35; H = 8·64.

$C_{16}H_{21}ON$ requires C = 79·00; H = 8·64 per cent.

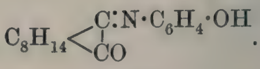
The reduction product is very freely soluble in organic media, including petroleum, and is slightly soluble in boiling water. A solution containing 0·0902 gram in 25 c.c. of chloroform gave α_D 0°55′ in the 2-dcm. tube, whence $[\alpha]_D$ 127·0°. It does not form a stable salt with platinum tetrachloride, which oxidises it, and attempts to prepare a benzoyl derivative by the Schotten-Baumann and pyridine methods were unsuccessful. The *nitroso*-derivative, $C_{16}H_{20}O_2N_2$, crystallised from dilute alcohol in faint yellow needles, becoming darker on exposure to light and air; it melted at 81—83°:

0·1282 gave 11·1 c.c. N_2 at 19° and 764 mm. N = 10·00.

$C_{16}H_{20}O_2N_2$ requires N = 10·30 per cent.

The substance is freely soluble in organic media, and gives Liebermann's reaction, but we have failed to convert it into camphorylphenylhydrazine.

p-*Hydroxyphenyliminocamphor*,



$C_8H_{14}\Big<\begin{array}{l}C\colon N\cdot C_6H_4\cdot OH\\ |\\ CO\end{array}.$

On mixing an alcoholic solution of camphorquinone with the calculated amount of *p*-aminophenol hydrochloride and sodium acetate in water, the colour of the liquid deepened, and after being gently heated during half an hour, yellow crystals separated. After recrystallisation from hot alcohol, the product was obtained in transparent, clear-cut, deep brown prisms, melting at 233° after sintering at about 220°:

0·1442 gave 0·3947 CO_2 and 0·0940 H_2O. C = 74·65; H = 7·24.

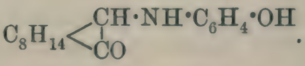
0·1689 ,, 8·3 c.c. N_2 at 19° and 761 mm. N = 5·71.

$C_{16}H_{19}O_2N$ requires C = 74·71; H = 7·39; N = 5·45 per cent.

Organic media dissolve the substance only sparingly, and it is insoluble in boiling petroleum. It is very slightly soluble in boiling water, but dissolves freely in sodium hydroxide, forming a deep red liquid, from which it is precipitated by acids; it dissolves also in sodium carbonate and in ammonia. Concentrated sulphuric and nitric acids dissolve it when cold without changing the colour, but when heated with hydrochloric acid the deep orange-yellow solution quickly becomes pale, and camphorquinone is precipitated on cooling. Ferric chloride has no action on an ethereal solution, but ferrous sulphate gives a bulky, grass-green precipitate when added to the solution in very dilute potassium hydroxide.

Action of Hydroxylamine.—In the hope of obtaining the oxime of *p*-hydroxyphenyliminocamphor, an alcoholic solution was mixed with slight excess over the calculated amount of hydroxylamine hydrochloride and sodium acetate dissolved in water, the red colour of the liquid disappearing completely in twelve hours. On removing alcohol without heating the solution, there separated *iso*nitrosocamphor, whilst *p*-aminophenol remained in the water. Camphorquinonedioxime was not produced.

p-*Hydroxyphenylaminocamphor*,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4\cdot OH\\ | \\ CO\end{matrix}.$$

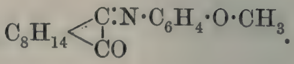
Reduction in this case was effected by shaking a solution of *p*-hydroxyphenyliminocamphor in dilute alkali hydroxide with zinc dust; if protected from air, the intense colour of the solution disappeared in a few minutes. The liquid was then saturated with carbon dioxide and extracted with ether, the colourless residue from this being recrystallised from dilute alcohol, which deposited minute prisms melting at 171°:

0·1642 gave 0·4503 CO_2 and 0·1221 H_2O. C = 74·79; H = 8·26.

$C_{16}H_{21}O_2N$ requires C = 74·13; H = 8·11 per cent.

The substance dissolves much more readily in organic media than the unreduced material, and crystallises from benzene in colourless, transparent prisms; it is even soluble, although slightly, in boiling petroleum, from which it separates in minute, colourless crystals. It dissolves in sodium carbonate, although not so freely as in alkali hydroxide, the liquid quickly becoming red in air. A solution containing 0·0978 gram in 25 c.c. of chloroform gave α_D 0°39′ in the 2-dcm. tube, whence $[\alpha]_D$ 83·1°.

p-*Methoxyphenyliminocamphor*,



$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_4\cdot O\cdot CH_3\\ |\\ CO\end{array}.$$

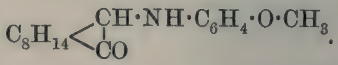
Condensation between camphorquinone and anisidine took place readily on the water-bath, and the product crystallised from alcohol in golden-yellow needles melting to a deep red liquid at 120°:

0·2027 gave 10·0 c.c. N_2 at 18° and 750 mm. N = 5·62.

$C_{17}H_{21}O_2N$ requires N = 5·20 per cent.

It is freely soluble in cold organic liquids, excepting petroleum, in which it dissolves readily on boiling, separating in long, flat, striated crystals when cold.

p-*Methoxyphenylaminocamphor*,



$$C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot C_6H_4\cdot O\cdot CH_3\\ |\\ CO\end{array}.$$

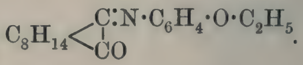
The reduction was attempted by the method used for phenyliminocamphor, but the ethereal solution did not lose its colour, and yielded unaltered material on evaporation. *p*-Methoxyphenyliminocamphor was therefore dissolved in glacial acetic acid and stirred with zinc dust until colourless; on diluting the filtered solution with water, colourless prisms separated slowly. After recrystallisation from alcohol, well-formed, transparent, six-sided prisms were obtained, melting at 101°:

0·1035 gave 0·2824 CO_2 and 0·0788 H_2O. C = 74·41; H = 8·46.

$C_{17}H_{23}O_2N$ requires C = 74·72; H = 8·42 per cent.

The substance dissolves very readily in organic media, and the yield is disappointing. A solution containing 0·0915 gram in 25 c.c. of chloroform gave α_D 0°30′ in the 2-dcm tube, whence $[\alpha]_D$ 68·3°.

p-*Ethoxyphenyliminocamphor*,



$$C_8H_{14}<\begin{array}{l}C{:}N\cdot C_6H_4\cdot O\cdot C_2H_5\\ |\\ CO\end{array}.$$

An aqueous solution of *p*-phenetidine hydrochloride mixed with sodium acetate was heated with the calculated amount of camphorquinone dissolved in alcohol; the liquid immediately darkened, and, after being heated during a few minutes on the water-bath, yielded a dense, yellow precipitate. Recrystallisation from alcohol, followed by petroleum, gave bright yellow, silky leaflets, melting at 112°. Much difficulty was experienced in estimating the nitrogen, which appears to be mixed with methane unless the combustion is performed with unusual deliberation:

0·1702 gave 7·9 c.c. N_2 at 18° and 767 mm. N = 5·41.

$C_{18}H_{23}O_2N$ requires N = 4·91 per cent.

Behaviour towards solvents resembled that of the methoxy-compound. On attempting to reduce *p*-ethoxyphenyliminocamphor, the product was an oil, alike whether an ethereal solution was shaken with aqueous potassium hydroxide and zinc dust, or whether the metal was added to a cold solution in glacial acetic acid. The solution of the oil in ether was saturated with dry hydrogen chloride, and the salt thus obtained decomposed with sodium carbonate and again precipitated with hydrogen chloride, the colourless substance decomposing at 210°:

0·2353 gave 0·1029 AgCl. Cl = 10·80.

$C_{18}H_{25}O_2N,HCl$ requires Cl = 10·94 per cent.

A solution containing 0·1880 gram in 25 c.c. of alcohol gave α_D 1°32′ in the 2-dcm. tube, whence $[\alpha]_D$ 101·9°. On setting free the base from this hydrochloride, however, it could not be obtained in crystals.

The Hydroxylamino-derivative.—Attempts to prepare an oxime from *p*-hydroxyphenyliminocamphor having failed, the ethoxy-derivative (5 grams) dissolved in alcohol was mixed with an aqueous solution of hydroxylamine hydrochloride (1·5 grams) and sodium acetate (3·5 grams); although the liquid was not heated, the yellow colour quickly faded, and after twelve hours the alcohol was removed under diminished pressure, leaving an oil which rapidly solidified. When thoroughly dry, this substance was dissolved in warm petroleum (b. p. 60—80°), and precipitated without delay by cooling, it having been found that the hydroxylamino-compound, although stable when dry, quickly changes to *iso*nitrosocamphor and phenetidine in the dissolved state; long, lustrous needles separated, melting at 63°:

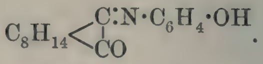
0·1155 gave 9·2 c.c. N_2 at 18° and 767 mm. N = 9·28.

$C_{18}H_{26}O_3N_2$ requires N = 8·80 per cent.

If the solution in petroleum is boiled and allowed to cool spontaneously, the long needles of the hydroxylamino-compound are mixed with transparent prisms melting at 152°, consisting of the stable *iso*nitrosocamphor, whilst the mother liquor contains phenetidine. Furthermore, alkali develops with the substance a yellow colour, due to *iso*nitrosocamphor, phenetidine being precipitated as an oil. Alcoholic ammoniacal silver oxide is reduced immediately on warming, and although this might certainly be due to initial resolution into phenetidine and *iso*nitrosocamphor, the latter substance and ethoxyphenyliminocamphor itself are not oxidised by this agent.

A solution containing 0·2209 gram in 20 c.c. of chloroform, and examined as quickly as possible, gave α_D 2°15′ in the 2-dcm. tube, whence $[\alpha]_D$ 101·8°, corresponding with $[M]_D$ 323·7°; slight increase occurred with lapse of time, rotation being constant at α_D 2°25′, corresponding with $[M]_D$ 347·9°, which approaches closely to that of the stable *iso*nitrosocamphor, 355·8°, in the same solvent.

m-*Hydroxyphenyliminocamphor*,



$$C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_4\cdot OH\\ | \\ CO\end{matrix}.$$

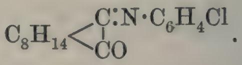
The product of condensation between camphorquinone and *m*-aminophenol was crystallised from alcohol, precipitated by petroleum from the solution in chloroform, and finally recrystallised from benzene, when it melted at 173·5°:

0·0707 gave 3·7 c.c. N_2 at 30° and 771 mm. N = 5·77.

$C_{16}H_{19}O_2N$ requires N = 5·45 per cent.

The substance is distinguished from the *p*-hydroxy-compound by its pale yellow colour and ready solubility in organic media; it is, however, insoluble in boiling petroleum. The solution in potassium hydroxide is orange-yellow, quite distinct in appearance from that of the isomeric substance.

p-*Chlorophenyliminocamphor*,



$$C_8H_{14}<\begin{matrix}C{:}N\cdot C_6H_4Cl\\ | \\ CO\end{matrix}.$$

Calculated amounts of *p*-chloroaniline and camphorquinone were heated together during four hours on the water-bath, and the hardened product recrystallised twice from alcohol, which deposited lustrous, flat, yellow prisms, melting at 140°:

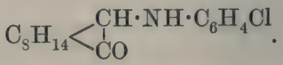
0·1070 gave 5·0 c.c. N_2 at 16° and 747 mm. N = 5·35.

0·2080 ,, 0·1070 AgCl. Cl = 12·70.

$C_{16}H_{18}ONCl$ requires N = 5·08; Cl = 12·85 per cent.

Cold organic liquids and hot petroleum dissolve it readily, the last-named depositing the substance in bundles of long, yellow needles on cooling.

p-*Chlorophenylaminocamphor*,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot C_6H_4Cl\\ | \\ CO\end{matrix}.$$

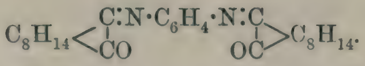
On adding zinc dust to a solution of *p*-chlorophenyliminocamphor in cold glacial acetic acid, the colour was discharged almost immediately; diluting the filtered liquid with water precipitated minute, snow-white crystals, and after recrystallisation from hot dilute alcohol, the substance was obtained in transparent, six-sided prisms, melting at 98°:

0·1269 gave 0·3245 CO_2 and 0·0854 H_2O. C = 69·74; H = 7·48.

$C_{16}H_{20}ONCl$ requires C = 69·21; H = 7·21 per cent.

The base is freely soluble, even in petroleum; a solution containing 0·0931 gram in 25 c.c. of chloroform gave α_D 0°42′ in the 2-dcm. tube, whence $[\alpha]_D$ 93·9°.

p-*Phenylenebisiminocamphor*,



$$C_8H_{14}\left<\begin{array}{l}C{:}N\cdot C_6H_4\cdot N{:}C\\ \mid \qquad\qquad\qquad\quad \mid\\ CO \qquad\qquad\qquad OC\end{array}\right>C_8H_{14}.$$

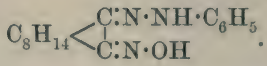
When alcoholic camphorquinone (2 mols.) was added to an aqueous solution of *p*-phenylenediamine hydrochloride mixed with excess of sodium acetate, an intense brown coloration was developed almost immediately, and after half an hour on the water-bath the cooled liquid deposited the condensation product. Crystallisation from boiling alcohol gave lustrous, golden-brown needles, melting to a deep red liquid at 259° :

0·2090 gave 13·6 c.c. N_2 at 23° and 773 mm. N = 7·46.

$C_{26}H_{32}O_2N_2$ requires N = 6·93 per cent.

The substance is freely soluble in chloroform and in pyridine, dissolving less readily in acetone, ethyl acetate, and benzene ; 1 gram requires about 50 c.c. of boiling alcohol to dissolve, and it is insoluble in petroleum. A solution containing 0·0840 gram in 20 c.c. of pyridine gave α_D 12°50′ in the 2-dcm. tube, whence $[\alpha]_D$ 1528°, corresponding with $[M]_D$ 6173° ; the rotatory power in chloroform, as already stated, is $[\alpha]_D$ 1509°, or $[M]_D$ 6096°. Attempts to reduce this compound have failed.

Oxime of Camphorquinonephenylhydrazone,



$$C_8H_{14}\left<\begin{array}{l}C{:}N\cdot NH\cdot C_6H_5\\ \mid\\ C{:}N\cdot OH\end{array}\right..$$

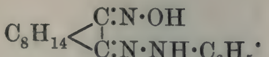
The difficulty of preparing oximes from α-derivatives of camphor has been the subject of comment, and camphorquinonephenylhydrazone is not an exception, but the method recently described for the production of α-benzilmonoxime (this vol., 431) proved successful in the present case. In a dry pyridine solution of hydroxylamine prepared from 10 grams of hydrochloride and 5·5 grams of sodium hydroxide, 4 grams of the camphor derivative were dissolved, and left at 40—50° during two months ; the silky, yellow needles which separated on pouring the liquid into a large volume of water were recrystallised from hot alcohol. Clear-cut, primrose-yellow, transparent prisms were obtained, melting at 195°, and depressing the melting point of camphorquinonephenylhydrazone when mixed with it :

0·1072 gave 14·5 c.c. N_2 at 21° and 771 mm. N = 15·63.

$C_{16}H_{21}ON_3$ requires N = 15·50 per cent.

A solution containing 0·2208 gram in 25 c.c. of alcohol gave α_D 2°36′ in the 2-dcm. tube, whence $[\alpha]_D$ 147·2°. All attempts to transform this compound into a structural isomeride of *iso*nitrosocamphor by removing the phenylhydrazine residue have been fruitless.

The Phenylhydrazone of iso*Nitrosocamphor*,



$C_8H_{14}<\begin{matrix}C:N\cdot OH\\ |\\ C:N\cdot NH\cdot C_6H_5\end{matrix}$.

This material was first prepared by Claisen and Manasse (*Annalen*, 1893, **274**, 78), and the suggestion has been made that it is derived from the unstable form of *iso*nitrosocamphor (m. p. 114°), because the stable modification, when separated from the Claisen mixture, fails to yield it (Trans., 1904, **85**, 909). If this were so it should be possible to recognise two isomerides, in which the configuration of the oximino-group corresponded to those of the two forms of *iso*nitrosocamphor. The condensation of *iso*nitrosocamphor (Claisen mixture) with phenylhydrazine was accordingly repeated without heating the materials, and the first precipitate, after being treated with a small quantity of cold alcohol and drained, was reprecipitated from a solution in cold chloroform by petroleum. Pale yellow needles, melting at 151° and having $[\alpha]_D$ $-235\cdot5°$ in alcohol, were obtained:

0·1155 gave 15·7 c.c. N_2 at 20° and 770 mm. N = 15·76.

$C_{16}H_{21}ON_3$ requires N = 15·50 per cent.

When the condensation product was extracted with boiling alcohol, however, the extract deposited primrose-yellow, transparent prisms, containing the same percentage of nitrogen, and melting at the same temperature, which was also the melting point of a mixture; but the specific rotatory power was $[\alpha]_D$ $-139\cdot5°$, which we regard as indicating the existence of two phenylhydrazones, and suppose that the one derived from the unstable *iso*nitrosocamphor passes readily into the phenylhydrazone of the stable form. The observation that the filtrate from the crude hydrazone yields the stable *iso*nitrosocamphor when extracted with alkali, is in agreement with the conclusion that it is the unstable form which is removed from the Claisen mixture by the condensing agent.

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CVI.—*The Colour of Aqueous Solutions of Violuric Acid.*

By FREDERICK GEORGE DONNAN and WILHELM SCHNEIDER, Ph.D.

SOME time ago, W. N. Hartley (Trans., 1905, **87**, 1797) called in question the fact that violuric acid, when dissolved in carefully purified water and guarded from contamination by alkalis, shows a violet-red colour. The statements of Hartley are entirely at variance with the work of Magnanini (*Atti. R. Accad. Lincei*, 1895, **4**, [ii], 60), Wagner (*Zeitsch. physikal. Chem.*, 1893, **12**, 314), Donnan (*Zeitsch. physikal. Chem.*, 1896, **19**, 465), and Guinchard (*Ber.*, 1899, **32**, 1723). Moreover, the statements of Hartley have been accepted without criticism by E. C. C. Baly (Trans., 1906, **89**, 979), who has made use of them in speculations on the constitution of violuric acid. In this state of affairs, it appears desirable to prevent this error from spreading further, although anyone acquainted with the literature of the subject would be scarcely likely to accept Hartley's statements without reserve. According to Hartley, previous investigators have been led astray by traces of alkali derived from glass vessels or from the air (ammonia). He succeeded in preparing a colourless (?) solution of violuric acid by dissolving the latter in water derived from pure ice melted in a vacuum, using only platinum vessels, and preventing any contamination from the air of the laboratory.

The following experiments have been carried out in order to demonstrate the erroneous nature of Hartley's observations and conclusions. Violuric acid was twice recrystallised from pure conductivity water, and then finally from some of this water which had been faintly acidified with a drop or two of hydrochloric acid. The solid acid was filtered, washed with the same acidified water, and dried in a platinum basin, or on pure filter paper at 100° until constant in weight. The dry acid was not allowed to come into contact with glass. It was put into a platinum dish, and water distilled directly into the latter from a distillation apparatus of metal (copper boiler and block tin condenser). The water in the boiler of the distillation apparatus was acidified with sulphuric acid. The solution of violuric acid so obtained showed the usual violet-red colour. Hartley attributes in his paper the most importance to an experiment in which the concentration of the violuric acid was only 0·15 gram per litre, that is, only about $N/1000$. We have carried out some experiments with solutions of such concentrations, and find that it is impossible to see any colour when the liquid reaches a height of only 2 to 3 cm. in a platinum crucible. When the height is 4 cm., a faint colour is just perceptible. Hartley does not mention the thickness of liquid he dealt with, and therefore it is not possible to say with certainty whether the above is the true explanation of his erroneous observations, but it is highly probable that this is the case.

It might be still possible to argue that the colour of the solution obtained as described above was due to slight contamination with ammonia from the air, although such an explanation is in the highest degree improbable, as the colour of the solution developed the moment the water dropped on to the solid acid from the tin condenser.

There is, however, a very simple way of disposing of this argument. The investigations of Donnan (*loc. cit.*) have shown that Arrhenius's theory of isohydric solutions can be applied to aqueous solutions of violuric acid mixed with other acids which do not yield coloured molecules or ions. This holds good in spite of the fact that, according to Hantzsch, we have to deal here with a case of ionisation-isomerism.* The explanation of this is probably due to there being comparatively little of the undissociated true acid present. Magnanini has shown that for the dissociation constant of violuric acid we have ($t=25°$) $k=2{\cdot}7\times10^{-5}$. Suppose now we have a $N/1000$-solution of hydrogen chloride; what should be the molar concentration (c) of a violuric acid solution, in order that the H$^{\cdot}$-ion concentration due to the violuric acid should equal that due to the hydrochloric acid? Let a = degree of dissociation of the violuric acid. We may assume the $N/1000$-solution of hydrogen chloride to be completely dissociated. We have then approximately:

$$a^2 = \frac{k}{c},$$

$$ac = 10^{-3},$$

whence

$$c = \frac{1}{27}.$$

It can be easily shown experimentally that the $N/1000$-solution of hydrogen chloride does not affect the depth of colour of the $N/27$-solution of violuric acid (looking through the total length of the solution all the time).

Still more conclusively, it is easy to show that if enough pure solid violuric acid be added to a $N/1000$-solution of hydrogen chloride to make it, say, about $N/30$ with respect to violuric acid, the mixed solution still shows a distinct violet-red colour. As the $N/1000$-solution of hydrogen chloride reacts strongly acid to litmus, and the pure yellow violuric acid has been recrystallised from a hydrogen chloride solution and preserved from contact with glass, the incorrectness of Hartley's conclusions will be evident.

If we accept Hantzsch's view that in an aqueous solution of violuric acid we have to deal with the equilibria, isomeric ψ-acid $\rightleftharpoons$ undissociated true acid $\rightleftharpoons$ ions, then the observations of Guinchard lead to the conclusion that the equilibrium shifts towards the colourless (or nearly colourless) ψ-acid with falling temperature.

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* Hantzsch's views have, however, been contested by H. Lundén (compare *Affinitätsmessungen an schwachen Säuren und Basen*, Ahrens' Sammlung, Bd. XIV, 1908).

The intensity of colour of the aqueous solutions of violuric acid diminishes with decreasing temperature. This fact may have contributed to Hartley's conclusion that the aqueous solutions are devoid of colour, for his solutions were obtained from melting ice, and must therefore have initially possessed a fairly low temperature.

Considering all the previous exact quantitative work that has been carried out on the colour of aqueous solutions of violuric acid, the conclusion of Hartley that this colour is due to accidental, and therefore variable, contamination with alkalis appears all the more extraordinary. It is to be hoped that the few simple experiments described in this paper will suffice to dispose of the very slender experimental evidence on which his conclusion was based.

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CVII.—*The Retarding Effect of Oxygen on the Rate of Interaction of Chlorine and Hydrogen.*

By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON.

BY the continued electrolysis of hydrochloric acid, a mixture of chlorine and hydrogen free from air is ultimately obtained. The sensitiveness of the mixture to light rises as the air is removed, and then, consequent on a decrease in the concentration of the acid, falls gradually. The slow fall in the sensitivenes is due, no doubt, to a comparatively small volume of oxygen liberated at the anode, and increasing in amount as the concentration of the acid becomes less. From the same cause, an increase in the density of the electrolysing current is accompanied by a depression in the sensitiveness of the evolved gases. Under the most favourable conditions for obtaining a sensitive mixture (when the current density is small and the concentration of the acid great), some oxygen is almost certainly evolved. Bunsen and Roscoe considered that electrolytic gas, free from oxygen and of constant sensitiveness, could be obtained by the electrolysis of concentrated hydrochloric acid; but, in point of fact (as we shall show later), electrolytic gas many times more sensitive than that investigated by Bunsen and Roscoe can be prepared, and there are strong reasons for thinking that if oxygen and other inhibitive impurities could be entirely removed the sensitiveness of the gas would be infinite.* The last conclusion is drawn from the results of a quantitative investigation on the inhibitive influence of oxygen on the rate of interaction of chlorine and hydrogen. It has been shown that for measurable amounts of oxygen the relation subsisting between the sensitiveness of the electrolytic gas and the volume of oxygen contained in unit volume of the mixed gases is closely expressed by the formula $[O] \times S = C$, where $[O]$ is the amount of oxygen per unit volume, S is the sensitiveness of the electrolytic gas, and C is a constant. If the above relation holds for infinitely small proportions of oxygen, then the sensitiveness of a pure mixture of chlorine and hydrogen would manifestly be infinite. In other words, chlorine and hydrogen would interact in the dark, provided that no oxygen or other inhibitive impurity were present.

The metastability of an explosive mixture of gases is commonly regarded as due entirely to the innate properties of the active constituents of the mixture, but there would now appear to be some grounds for believing that in the case of a mixture of chlorine and hydrogen, at any rate, the presence of inhibitive impurities is a necessary condition of "false equilibrium."

An interesting conclusion, concerning the influence of moisture on the inhibitive effect of oxygen, can be drawn by considering the connexion between the known effect of moisture and the above relation. H. B. Dixon has shown that as moisture is removed from electrolytic gas prepared from hydrochloric acid the sensitiveness falls. From this result, it follows that the constant C in the formula $[O] \times S = C$ is reduced by drying the mixture, and therefore the addition of a small amount of oxygen to two mixtures—one partly dry and the other moist—of chlorine and hydrogen free from oxygen would depress the sensitiveness of the dried mixture to a much lower value than it would that of the moist.

The electrolytic cell was similar to that described in a previous communication (this vol., p. 135). It was almost completely immersed in water contained in a metal-bath, and, if desired, the temperature of the water in the bath could be raised to the boiling point. To destroy ammonia and albuminoid substances contained in the electrolyte, the acid was saturated with chlorine, and the cell was maintained at a temperature of 100° for several days until the chlorine and hydrogen resulting from the electrolysis of the acid interacted almost immediately on exposure to light. During the electrolysis of the acid, the cell was maintained at a constant temperature. The device for adding a measured quantity of air or oxygen to the actinometer is depicted in the accompanying figure. The mixture of hydrogen and chlorine was first passed through the taps *a* and *b*, and the insolation vessel of the actinometer until all the air had been displaced from the cell and the actinometer. The tap *c* was then opened, and the electrolytic gas was allowed to escape through the potassium hydroxide solution in the beaker *x*. The taps *a* and *b* were next simultaneously turned, so that the tubes *m* and *n* were placed in communication, and a current of air or oxygen was passed from *m* to *n* until all the electrolytic gas in the tube between the taps *a* and *b* had been displaced. The tap *c* was then closed, and the taps *a* and *b* were turned, so that the electrolytic gas again passed into the actinometer. When a volume of gas just sufficient to drive back the liquid in the index of the actinometer had been admitted to the insolation vessel, the tap *a* was again turned so as to enable the hydrogen and chlorine to escape through the tube *m*. The volume of electrolytic gas thus admitted to the actinometer was more than sufficient to drive all the air enclosed between the taps *a* and *b* into the actinometer. Several measurements of the sensitiveness were made after each addition of air or oxygen, and the means of these are given in the table below. The standard light employed was a one-candle power Hefner amyl acetate lamp, which was carefully protected from draughts. To prevent any leakage of air into the electrolytic cell through the taps and ground-glass joints when the cell was not actually in use, a current of about 0·01 ampere was continuously conducted through it, the evolved gases being allowed to escape through the potassium hydroxide solution in the beaker *x*. The arrangements for main-

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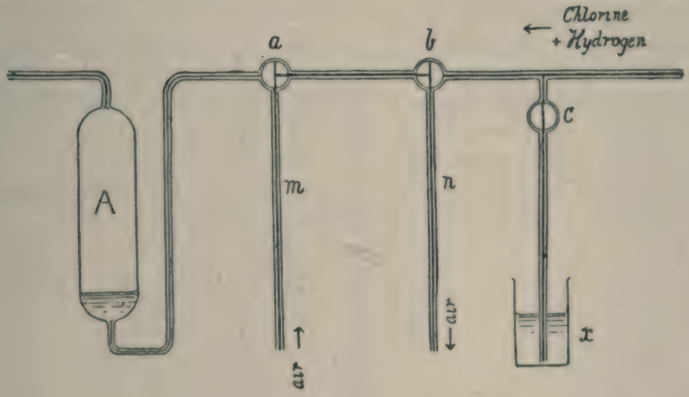
* We have already succeeded in preparing electrolytic gas at least five times more sensitive than that obtained by Bunsen and Roscoe.



taining the pressure and temperature in the actinometer constant were the same as those employed by Burgess and Chapman (Trans., 1906, **89**, 1426).

The volume of the insolation vessel, an allowance being made for the liquid contained in it, was 86·2 c.c., and the volume of the capillary tube between the taps *a* and *b* was 0·352 c.c.

The Influence of Nitrogen.—To test the influence of nitrogen, the space between *a* and *b* was filled with atmospheric nitrogen, from which the oxygen had been removed with great care, and this nitrogen was then driven into the insolation vessel of the actinometer. The values of the sensitiveness before and after the addition of the nitrogen were 3·60 and 3·52 respectively. An equal volume of air was then admitted to the actinometer, and the sensitiveness was thereby reduced to 0·26. From this result, we conclude that the inhibitive influence of air must be ascribed to the oxygen contained in it, and that the effect, if any, of the nitrogen can be neglected.

The Inhibitive Influence of Oxygen.—The effect of admitting successive volumes of oxygen to the insolation vessels are recorded in the following table. In the first column of the table the volumes of oxygen contained in 100 c.c. are given, and in the second and third columns the corresponding values of the sensitiveness and the product: sensitiveness × volume of oxygen per 100 c.c.:

Oxygen in 100 c.c.	Sensitiveness.	[O] × S.
—	2·58	—
0·0858	0·2507	0·02151
0·1004	0·2172	0·02181
0·1862	0·1218	0·02268
0·5946	0·0389	0·02311
1·0030	0·0268	0·02685
	Mean =	0·02319

It will be immediately perceived that the oxygen contained in our electrolytic gas must have been considerably less than that contained in the gas prepared by Bunsen and Roscoe, for an addition of less than one part of oxygen in a thousand reduced the sensitiveness of our mixture in almost the same ratio as an addition of as much as five parts of oxygen in a thousand reduced that of Bunsen and Roscoe. Moreover, the electrolytic gas used in the last recorded experiment was by no means the most sensitive specimen which can be prepared, that employed to investigate the influence of nitrogen being more sensitive in the ratio of 3·6 to 2·6.

If it is assumed that as a first approximation the product [O] × S is a constant equal to 0·0232, it becomes possible to calculate the volume of oxygen in 100 c.c. of the original mixture. Let this amount of oxygen be x.

$$\text{Then } 2{\cdot}58 \times x = 0{\cdot}0232,$$

whence $x = 0{\cdot}0090$, or approximate one volume in ten thousand. On the assumption that the original gas contained this amount of oxygen, the values of $[O] \times S$ have been calculated, and are recorded in the table below:

Oxygen in 100 c.c.	Sensitiveness.	[O] × S.
0·0090	2·58	0·0232
0·0948	0·2507	0·0237
0·1094	0·2172	0·0237
0·1951	0·1218	0·0238
0·6036	0·03887	0·0235
1·012	0·02685	0·0272

It is not improbable that the value of the product $[O] \times S$ may rise slowly as the amount of oxygen is increased, and if this should prove on further investigation to be the case, the chances of the sensitiveness of a pure mixture of moist chlorine and hydrogen being infinite would manifestly be increased. At the present time, attempts are being made to prepare mixtures of chlorine and hydrogen of greater sensitiveness than any which have hitherto been obtained and examined, and experiments are in progress for the purpose of testing our conjecture that the inhibitive influence of oxygen increases as moisture is removed.

We will now consider briefly the bearing of the relation disclosed in this paper on the theory advanced by Burgess and Chapman (Trans., 1906, **89**, 1433) to account for photochemical inhibition. The hypothesis in question assumes that the light absorbed by the chlorine is not immediately degraded into heat, but is, as it were, stored up as efficient energy in the molecules of chlorine. The union with hydrogen takes place by reason of this stored-up energy, and the rate of chemical change is, *ceteris paribus*, proportional to the amount of efficient energy accumulated. An inhibitor is supposed to discharge the efficient energy of the chlorine, which loses thereby its power of uniting with hydrogen.*

Consider a volume element of the mixture illuminated by monochromatic light of intensity I. Let x represent the efficient energy accumulated in the molecules of chlorine, and o the quantity of oxygen in the same element of volume. The rate of decrease of

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* The fact that neither iodine vapour nor anthracene vapour can be made to fluoresce when oxygen is present demonstrates that oxygen does, in certain cases, accelerate the degradation of energy derived directly from the light and stored in the molecules.

We have endeavoured to show, but without success, that chlorine, free from oxygen, will fluoresce.

x or $-\dfrac{dx}{dt}$ due to the discharge of the efficient energy by the oxygen will obviously be proportional both to x and to o, or

$$-\frac{dx}{dt} = k_1xo,$$

where k_1 is a constant.

Also the rate of increase of x resulting from the light absorbed will be proportional to the intensity of the light, or

$$\frac{dx}{dt} = k_2I,\text{*}$$

but the loss and gain of x are equal.

Therefore $$k_2I = k_1xo$$

or $$x = \frac{k_2}{k_1}\frac{I}{o}.$$

The efficient energy accumulated in the chlorine is directly proportional to the intensity of the light, and inversely proportional to the oxygen present. From which it follows that the rate of chemical change is proportional to the intensity of illumination and inversely proportional to the oxygen present.

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CVIII.—*An Examination of Irritant Woods. Part I. Chloroxylonine from East Indian Satinwood.*

By S. J. MANSON AULD, D.Sc.(Lond.), Ph.D.

THERE are at present two different kinds of satinwood in use in Great Britain—East Indian satinwood, derived from *Chloroxylon swietenia*, and West Indian or San Domingo satinwood, the product of *Fagara flava*. The woods are chiefly employed for veneering purposes and the manufacture of ornamental articles, as they have a very beautiful appearance, and are capable of taking a high polish. Although much alike in appearance, they do not seem to have any botanical relationship. Both species have been reported at different times to possess poisonous characteristics, but this has only been verified in independent cases for West Indian satinwood.

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* It may not be evident, at first sight, why it is assumed that the rate of increase of x is dependent only on the intensity of illumination and independent of the magnitude of x. On a priori grounds, the assumption would not be legitimate; but its validity rests on the fact established by Burgess and Chapman (Trans., 1906, **89**, 1429) that the coefficient of absorption of chlorine is uninfluenced by the presence of oxygen. The rapidity with which the energy is dissipated is so rapid that x is too small to influence the rate of conversion of light energy into the above-mentioned efficient energy of the chlorine molecules.

A few years ago several cases of poisonous irritation of the skin of men working at a Glasgow saw-mill were brought to the notice of Dr. H. E. Jones, of Ibrox, Glasgow, who traced them to the satinwood which the men were engaged in cutting. At the instance of Mr. James Whitton, Curator of the Botanic Gardens, Glasgow, samples of the two satinwoods, both of which were in use, were forwarded to the Imperial Institute for examination, together with an accompanying note stating that both produced the irritable eruption, but that one, the East Indian satinwood, was more virulent than that from San Domingo. The East Indian wood was consequently first examined. No previous cases of the production of poisonous effects have been recorded with regard to this wood, and it has since been frequently stated to be quite harmless (compare Jones, *Brit. Med. Journ.*, June 25th, 1904; Grabham, *ibid.*, April 15th, 1905; Bidie, *ibid.*, January 14th, 1905).

The East Indian satinwood tree, *Chloroxylon swietenia*, D.C., grows largely in Central and Southern India and Ceylon. The wood is not now much exported to Europe, owing to the competition of the West Indian wood, which is cheaper and more plentiful.

Preliminary Examination.

For extraction, the wood was converted into sawdust, and this was exhausted severally with light petroleum, water, dilute hydrochloric acid, and strong alcohol. By this means the presence was shown in the wood of calcium oxalate in fair quantity, a peculiar protein compound, two inert resins, a fixed oil, and an alkaloid. The oil after purification was found to be rather viscous and yellowish-brown in colour; the specific gravity is 0·965, and it remains perfectly clear on keeping. It is present to the extent of about 1 per cent. in the wood as received, and does not appear to possess irritant properties.

Extraction of the Alkaloid.

Owing to the comparatively small quantity of the alkaloid present in the wood, it is necessary to employ large quantities for its separation. The sawdust is thoroughly exhausted by continued percolation with 90 per cent. alcohol, and the spirit removed from the percolate by distillation under slightly diminished pressure. The remaining viscid, resinous mass is then exhausted several times with dilute (2 per cent.) hydrochloric acid. Finally, the resin is dissolved in dilute aqueous potassium hydroxide, and the residue, after filtration, is exhausted several times with dilute acid and the solution added to the main acid extract. The resin is precipitated from solution by the addition of acid, and the filtrate again added to the bulk of the extract. The alkaloid is now liberated by the addition of dilute ammonia solution, and extracted thoroughly by repeated treatment with ether. On evaporating the dried ethereal solution, crusts of prismatic crystals separate. These are collected and recrystallised from absolute alcohol or chloroform. A further supply of the material may be obtained from the mother liquors.

As the base cannot be identified with any known alkaloid, it is proposed to give it the name *chloroxylonine*.

Properties of Chloroxylonine.

Chloroxylonine is best crystallised from ethyl alcohol, in which it is fairly soluble. The crystals are well-defined prisms, and probably belong to the monoclinic system. Crystals, often large and well-defined, may also be obtained from chloroform, in which the alkaloid very readily dissolves, but the crystals rapidly effloresce and lose one molecule of chloroform of crystallisation, becoming amorphous and opaque.

The purified base melts at 182—183°. It is soluble in dilute acids, and may be re-precipitated by ammonia, dissolving again in excess of the latter. It reacts neutral towards litmus. Concentrated sulphuric acid dissolves the alkaloid without producing any coloration:

0·1505 gave 0·3555 CO_2 and 0·0698 H_2O. $C=64·4$; $H=5·2$.
0·2035 „ 0·4790 CO_2 „ 0·0971 H_2O. $C=64·1$; $H=5·3$.
0·1370 „ 7·3 c.c. N_2 (moist) at 20° and 760 mm. $N=3·2$.
$C_{22}H_{23}O_7N$ requires $C=63·9$; $H=5·5$; $N=3·3$ per cent.

Using Perkin's modification of Zeisel's method, it was found that the alkaloid contains four methoxyl groups:

0·1615 gave 0·3745 AgI. OMe = 30·58.
0·2285 „ 0·5283 AgI. OMe = 30·50.
$C_{18}H_{11}O_3N(OMe)_4$ requires OMe = 30·02 per cent.

The residual clear liquid obtained after boiling chloroxylonine with hydriodic acid was diluted with much water, whereby a flocculent precipitate was obtained. After filtering and washing, it was dissolved in alcohol, and again precipitated with water.

The substance is apparently the unreduced hydroxy-alkaloid, $C_{18}H_{11}O_3N(OH)_4$. It forms a yellow powder, which gradually changes on standing to a slate grey, and finally to a purple shade. It melts and decomposes at about 285°, and dissolves readily in strong acids, being re-precipitated by water. Alkalis dissolve it with a bright green colour. It is soluble in most of the ordinary organic solvents:

0·0980 gave 0·2158 CO_2 and 0·0388 H_2O. C = 60·8; H = 4·4.

$C_{18}H_{15}O_7N$ requires C = 60·5; H = 4·2 per cent.

The optical rotation of chloroxylonine was measured in chloroform solution at 18° for a 4·6640 per cent. solution. The substance is lævorotatory, and the mean of a dozen readings gave $[\alpha]_D^{18}$ $-9°18'$. The solution of chloroxylonine in dilute mineral acids is also lævorotatory.

Salts of Chloroxylonine.

Chloroxylonine is a mono-acidic base, and as such forms a mono-hydrochloride, hydrobromide, etc. The alkaloid is only very weakly basic in character, and as most of its salts dissociate in aqueous solution, it is impossible to prepare them by dissolving the base in a dilute solution of the acid; indirect methods were therefore employed.

Chloroxylonine Hydrochloride, $C_{22}H_{23}O_7N,HCl$.—As evaporation of a solution of chloroxylonine in dilute hydrochloric acid invariably produces varnishes, the alkaloid is dissolved in perfectly dry chloroform, and a dry chloroform solution of hydrogen chloride added in slight excess, the mixture being kept cool with ice. After keeping for several hours in a stoppered vessel, the solution is allowed to evaporate gradually, when the hydrochloride separates in rosettes of a beautiful slightly green substance crystallising in long needles and melting at about 95°:

0·1145 gave 0·0359 AgCl. Cl = 7·8.

$C_{22}H_{24}O_7NCl$ requires Cl = 7·9 per cent.

On the addition of water, the hydrochloride decomposes into hydrogen chloride and the free base, the latter dissolving again on addition of more acid.

Chloroxylonine Hydrobromide.—The hydrobromide is prepared in a similar manner to the hydrochloride. It crystallises from chloroform in prismatic needles melting at 125°.

Chloroxylonine Nitrate, $C_{22}H_{23}O_7N,HNO_3$.—To prepare this salt, the calculated quantity of silver nitrate, dissolved in absolute alcohol, is added to the alkaloid hydrochloride also dissolved in absolute alcohol. After warming slightly for a short time, the precipitated silver chloride is collected, and the solution allowed to cool. The nitrate separates out almost at once as a bulky, white mass of long, fibrous crystals. These are collected, washed with absolute alcohol, and dried on porous tile. After recrystallisation, the nitrate forms a beautiful white, microcrystalline substance, which decomposes on heating at 150—160°. It dissolves in most of the ordinary solvents:

0·1230 required 0·0101 NaOH. $HNO_3 = 13·0$.

$C_{22}H_{23}O_7N,HNO_3$ requires $HNO_3 = 13·2$ per cent.

Chloroxylonine aurichloride, $C_{22}H_{23}O_7N,HAuCl_4$, is obtained by the gradual addition of gold chloride to the solution of the base in dilute hydrochloric acid. The double salt is immediately precipitated as a bulky, crystalline mass, and, after recrystallising from dilute alcohol, is obtained in reddish-yellow groups of needles melting at 70°. The aurichloride is very soluble in warm water, more sparingly so in the cold solvent. It also dissolves readily in alcohol:

0·1747 gave 0·0470 Au and 0·1313 AgCl. Au = 26·7; Cl = 18·6.

$C_{22}H_{24}O_7NCl_4Au$ requires Au = 26·2; Cl = 18·8 per cent.

Action of Acetic Anhydride on Chloroxylonine.

Several attempts to prepare an acetyl compound from chloroxylonine all resulted in failure, the original alkaloid being readily obtainable from its solution in acetic anhydride even after boiling for six hours. From this, it must be concluded that chloroxylonine contains no free hydroxyl groups.

Unfortunately for the success of the investigation, further large supplies of the East Indian satinwood which were obtained were found to contain only very small quantities of the alkaloid. A more detailed account of chloroxylonine is therefore indefinitely postponed until larger quantities of material are available.

The physiological action of chloroxylonine is at present being fully investigated by Professor Cash, of Aberdeen University, and there seems little doubt that in certain circumstances the alkaloid is capable of producing dermatitis similar in character to that ascribed to the wood itself.

The author wishes to thank Professor W. R. Dunstan, F.R.S., for permission to publish the results of this investigation.

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CIX.—*Contributions to the Chemistry of the Terpenes. Part V. The Action of Chromyl Chloride on Terpinene and on Limonene.*

By GEORGE GERALD HENDERSON and WILLIAM CAMERON.

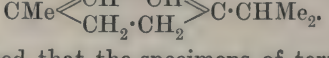
IN continuation of the investigation of the products formed by the action of chromyl chloride on terpenes, of which accounts have already been communicated to the Society (Trans., 1903, **83**, 1299; 1907, **91**, 1871; 1908, **93**, 288), we have recently examined the behaviour of terpinene towards that oxidising agent, with somewhat unexpected results. When a dilute solution of chromyl chloride (2 mols.) in dry carbon disulphide is added slowly to terpinene (1 mol.) largely diluted with the same solvent, there is considerable evolution of heat, and a solid compound separates. The solid is of a greyish-brown colour when dry, and on exposure to air quickly takes up moisture and undergoes decomposition. On treatment with water, it yields an insoluble, brown, oily liquid of an aromatic odour, while chromic chloride passes into solution. When this liquid oxidation product, after purification by distillation with steam, is mixed with a saturated solution of sodium hydrogen sulphite, about one-half remains unattacked, and the rest forms a bisulphite compound, which separates quickly in small, pearly plates. From this compound an aldehyde of the formula $C_{10}H_{12}O$ was prepared in the usual manner. Investigation of the properties of the aldehyde led to the conclusion that it is not the expected derivative of terpinene, but is, indeed, no other than α-*p*-tolylpropaldehyde, $C_6H_4Me{\cdot}CHMe{\cdot}CHO$. It has already been shown by Errera (*Gazzetta*, 1889, **19**, 528; 1891, **21**, 76) and by Miller and Rohde (*Ber.*, 1890, **23**, 1070; 1891, **24**, 1356) that this aldehyde is one of the substances produced by the action of water on the solid compound, $C_{10}H_{14},2CrO_2Cl_2$, which is formed when a dilute solution of cymene in carbon disulphide is treated with a similar solution of chromyl chloride.

The portion of the liquid oxidation product which did not react with sodium hydrogen sulphite was washed with water, dried, and fractionally distilled under diminished pressure, with the result that three distinct liquid substances were separated from it. The liquid of lowest boiling point, of which the quantity was small, was proved to be cymene. The sound fraction, which was also a very small one, contained an oxidation product of the formula $C_9H_{12}O$, which presumably is a ketone, since it forms a semicarbazone. The third compound, which was present in by far the largest proportion, was found to be a ketone of the formula $C_9H_{10}O$, and was ultimately identified as *p*-tolyl methyl ketone, $COMe\cdot C_6H_4Me$. This ketone has also been obtained from cymene by Errera and by Miller and Rohde, being produced along with *a*-*p*-tolylpropaldehyde by the action of water on the additive compound, $C_{10}H_{14},2CrO_2Cl_2$.

According to these results, terpinene on oxidation with chromyl chloride yields the same chief products as are formed by treatment of cymene with that reagent. It might therefore appear not improbable that the hydrocarbon employed in our experiments was in reality cymene, and not terpinene; that, however, was not the case. We used for oxidation two different specimens of terpinene. One of these, supplied by Schuchardt, was presumably prepared from pinene by the usual process of treatment with sulphuric acid. To obtain the other we used the method of Genvresse (*Compt. rend.*, 1902, **134**, 360), according to which pinene was heated for some time with about one-fourth of its weight of crystallised arsenic acid, the mixture then subjected to distillation in a current of steam, and the terpinene collected, dried, and distilled. Before use each specimen was carefully distilled through a "pear" fractionating column, and only the fraction which boiled at 179—181° was used for oxidation. Other physical properties of this fraction were determined, with the following results:

$$d_{20^\circ}^{20^\circ} = 0\cdot845\ ;\ n_D = 1\cdot48521\ ;\ \text{mol. refract. } 45\cdot6.$$

Moreover, the liquid resinified quickly on standing, and, when treated with nitrous acid, readily gave a copious yield of the characteristic crystalline terpinene nitrosite, melting at 155°. There is no doubt that the substance in our hands was ordinary terpinene, which, according to Wallach (*Annalen*, 1908, **362**, 285), is mainly composed of *a*-terpinene,



$$CMe{<}\begin{matrix}CH{-}CH\\CH_2\cdot CH_2\end{matrix}{>}C\cdot CHMe_2.$$

It must also be noted that the specimens of terpinene cannot have contained more than a very small proportion of cymene, and yet the yields of *a*-*p*-tolylpropaldehyde and of *p*-tolyl methyl ketone obtained from them were not very far from being quantitative. In short, it is impossible to account for the formation of such quantities of these compounds on the supposition that they were directly derived from cymene present as an impurity in the terpinene.

Our experiments, therefore, have shown that chromyl chloride acts quite differently on terpinene on the one hand, and on pinene and camphene on the other. Each of the latter hydrocarbons yields an additive compound of the formula $C_{10}H_{16},2CrO_2Cl_2$;

terpinene, on the contrary, is, for the most part, first oxidised to cymene, and the cymene then reacts with the chromyl chloride to form the compound $C_{10}H_{14},2CrO_2Cl_2$. Probably a small proportion of the terpinene is at the same time converted into a compound, $C_{10}H_{16},2CrO_2Cl_2$, which on treatment with water yields the ketone $C_9H_{12}O$ referred to above.

In the course of this work we were struck with the resemblance between the properties of the aldehyde and of the ketone formerly obtained by oxidising limonene with chromyl chloride (Trans., 1907, **91**, 1871), and of the *α-p*-tolylpropaldehyde and *p*-tolyl methyl ketone respectively, which were similarly formed from terpinene. In particular, the semicarbazones of the two aldehydes and ketones exhibited this resemblance in a striking manner. The aldehyde derived from limonene was found to boil at 221—222°/755 mm., and its semicarbazone to melt at 156°; *α-p*-tolylpropaldehyde boils at 222° under atmospheric pressure, and its semicarbazone melts at 155°; the melting point of a mixture of the two semicarbazones was the same. Former analyses of the limonene aldehyde gave results which agreed rather better with the figures calculated for the formula $C_{10}H_{14}O$ than with those corresponding with the formula $C_{10}H_{12}O$, but, on the other hand, determinations of the percentage of nitrogen in its semicarbazone favoured the adoption of the latter formula. In their other properties the two aldehydes agree fairly closely, the only notable difference observed between them being that the limonene aldehyde underwent partial oxidation on exposure to air, yielding a small proportion of a crystalline acid, whilst the other does not appear to oxidise at all readily in these circumstances. Taking the available evidence into account, we conclude that the aldehyde derived from limonene consists for the most part of *α-p*-tolylpropaldehyde, but that a small proportion of a different aldehyde is mixed with this. The two ketones also resemble each other closely. The ketone derived from limonene was found to boil at about 112°/20 mm., whilst *p*-tolyl methyl ketone boils at about 109°/14 mm. The semicarbazone of each ketone crystallises with 1 mol. of methyl alcohol, which is quickly lost on exposure to air; after heating at 100° to expel methyl alcohol, each semicarbazone melts at 204—205°, and a mixture of the two compounds melts at the same temperature. Analysis of the limonene ketone gave results which pointed to the formula $C_9H_{12}O$ rather than to $C_9H_{10}O$; but the percentage of nitrogen contained in its semicarbazone agreed closely with that calculated for the corresponding derivative of a ketone of the formula $C_9H_{10}O$. Hence it appears that the ketone derived from limonene is *p*-tolyl methyl ketone.

Limonene, therefore, when treated with chromyl chloride under the conditions formerly described, is, to a large extent at least, oxidised to cymene, which then forms the solid, $C_{10}H_{14},2CrO_2Cl_2$. While resembling terpinene in this respect, it differs considerably from the latter in other ways. As already stated, the yields of *a-p*-tolylpropaldehyde and *p*-tolyl methyl ketone obtained from terpinene are very good, but the solid compound derived from limonene gives, on treatment with water, much resinous matter and only very small quantities of the aldehyde and the ketone. Further, more than half of the oxidation product of terpinene is composed of the aldehyde, while the ketone is the chief constituent of the liquid obtained from limonene.

EXPERIMENTAL

The method of preparing and decomposing the solid produced by the action of chromyl chloride on terpinene was essentially the same as that employed in the case of pinene and limonene, which has already been described (Trans., *loc. cit.*). The brown, oily liquid formed by treatment of the solid compound with water was purified by distillation in a current of steam, almost the whole quantity passing over, and only a little resinous matter being left in the flask. The purified liquid, now in the form of a clear, yellow oil, was mixed with a saturated solution of sodium hydrogen sulphite, and the bisulphite compound, which crystallised quickly in lustrous, pearly leaflets, was collected with the aid of the pump and washed with alcohol and with ether. The part of the liquid oxidation product which remained was treated repeatedly with the sodium hydrogen sulphite solution until no more crystals were formed, and as a result it was found that fully one-half of the original liquid consisted of an aldehyde. The bisulphite compound was heated with sodium carbonate solution in a current of steam, the aldehyde extracted from the distillate with ether, the ethereal solution washed, dried, evaporated, and the aldehyde finally purified by distillation under diminished pressure in a current of dry carbon dioxide. The aldehyde thus prepared is a colourless liquid with a peculiar odour. Its boiling point is 222° at atmospheric pressure; $d_{20^\circ}^{20^\circ} = 0{\cdot}984$; $n_D = 1{\cdot}51436$; mol. refract. $= 45{\cdot}3$. It is practically insoluble in water, but freely soluble in alcohol or ether, and it exhibits the characteristic properties of aldehydes. Oxidation does not take place at all readily when it is exposed to air. Analysis showed the formula of the compound to be $C_{10}H_{12}O$:

0·2576 gave 0·7654 CO_2 and 0·1886 H_2O. $C = 81{\cdot}04$; $H = 8{\cdot}14$.

0·3080 gave 0·9130 CO_2 and 0·2230 H_2O. C = 80·84; H = 8·05.
$C_{10}H_{12}O$ requires C = 81·0; H = 8·1 per cent.

The semicarbazone of the aldehyde, $C_{10}H_{12}\colon N\cdot NH\cdot CO\cdot NH_2$, crystallises in small, colourless prisms, which melt at 155°. It is readily soluble in cold, very easily so in hot, methyl alcohol:

0·1156 gave 19·9 c.c. N_2 at 16° and 767 mm. N = 20·8.
0·1345 „ 23·8 c.c. N_2 „ 17° „ 764 mm. N = 20·6.
$C_{11}H_{15}ON_3$ requires N = 20·5 per cent.

The properties of this aldehyde correspond precisely with those of *α-p*-tolylpropaldehyde, $C_6H_4Me\cdot CHMe\cdot CHO$, and the two substances behave in the same manner towards oxidising agents. By heating for a considerable time with silver oxide, each is converted into the corresponding *α-p*-tolylpropionic acid, $C_6H_4Me\cdot CHMe\cdot CO_2H$, small, colourless crystals which melt at 41—42°; when boiled with dilute nitric acid, each is oxidised to *p*-toluic acid, and when oxidised with potassium permanganate each yields terephthalic acid. In short, there can be no doubt that the aldehyde obtained by oxidising terpinene with chromyl chloride is *α-p*-tolylpropaldehyde, or, in other words, is a derivative of cymene and not of terpinene.

The ethereal solution of that part of the liquid oxidation product of terpinene which remained after the removal of the aldehyde by means of sodium hydrogen sulphite was washed, dried, and evaporated. The residual liquid was fractionally distilled under diminished pressure in a current of dry carbon dioxide, and after several distillations yielded three fractions of almost constant boiling point, whilst a small quantity of a thick residue containing some chlorinated product was left. The chief constituent was a colourless, rather oily liquid with a pleasant odour, which distilled at 109°/14 mm., and showed the character of a ketone. Several concordant analyses gave results agreeing fairly well with those required by the formula $C_9H_{10}O$, but as the compound was not quite pure but contained traces of a chlorinated product of which the separation was troublesome, its semicarbazone was prepared and analysed. These analyses left no doubt that the formula of this ketone is $C_9H_{10}O$.

The semicarbazone of the ketone, $C_9H_{10}\colon N\cdot NH\cdot CO\cdot NH_2$, crystallises from methyl alcohol in lustrous, colourless prisms containing one molecule of alcohol of crystallisation, which quickly become opaque and break down to a powder on exposure to air. After being heated for some time at 100°, the melting point of the semicarbazone is 204—205°. It is not readily soluble in hot, and very sparingly so in cold, methyl alcohol:

0·1370 gave 26·6 c.c. N_2 at 18° and 760 mm. $N = 22·4$.
0·1420 ,, 27·1 c.c. N_2 ,, 17° ,, 762 mm. $N = 22·2$.
$C_{10}H_{13}ON_3$ requires $N = 22·0$ per cent.

To determine the proportion of alcohol of crystallisation, a quantity of the crystals was quickly dried with filter paper, weighed, and heated at 100°:

0·3670 lost 0·0520. $MeOH = 14·1$.
$C_{10}H_{13}ON_3,MeOH$ requires $MeOH = 14·4$ per cent.

The phenylhydrazone of the ketone was also prepared. It crystallises from dilute alcohol in delicate, colourless needles, which melt at 88—89°.

The properties of the ketone, $C_9H_{10}O$, obtained by the oxidation of terpinene, as well as those of its semicarbazone and phenylhydrazone, agree so closely with the properties of *p*-tolyl methyl ketone, $COMe·C_6H_4Me$, and of its corresponding derivatives, that there can be no doubt as to the identity of the two compounds.

The other two substances separated from the ketone by fractional distillation constituted only a small proportion of the mixture. The first of these, a colourless liquid which boiled at 176° under atmospheric pressure, proved to be cymene, probably some of that formed from the terpinene, which had escaped further oxidation owing to part of the chromyl chloride having been consumed in converting the terpinene into cymene. The other substance, which distilled at 100°/14 mm., is a colourless liquid with a strong odour somewhat like that of peppermint. It appears to be a *ketone*, since it readily forms a crystalline semicarbazone. Although the quantity was too small to permit of thorough purification of the substance, the results of analysis agreed fairly well with those calculated for the formula $C_9H_{12}O$:

0·2604 gave 0·7530 CO_2 and 0·2048 H_2O. $C = 78·86$; $H = 8·74$.
0·2398 ,, 0·6962 CO_2 ,, 0·1890 H_2O. $C = 79·15$; $H = 8·75$.
$C_9H_{12}O$ requires $C = 79·4$; $H = 8·8$ per cent.

The *semicarbazone* of this ketone, $C_9H_{12}{:}N·NH·CO·NH_2$, crystallises from alcohol in very small, colourless prisms, which melt at 200—201°. It is only sparingly soluble in alcohol:

0·1158 gave 22·3 c.c. N_2 at 19° and 754 mm. $N = 21·9$.
$C_{10}H_{15}ON_3$ requires $N = 21·8$ per cent.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which met the cost of the materials used.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CX.—*Esterification Constants of Substituted Acrylic Acids. Part IV.*

By **John Joseph Sudborough** and **Morton James Pryce Davies**.

In continuation of the work on the esterification of acrylic acid derivatives (Trans., 1898, **73**, 81; 1905, **87**, 1840; 1907, **91**, 1033; this vol., 315), we have determined the rates of esterification of the various methyl-substituted derivatives of acrylic acid, and the results obtained are recorded in the present paper.

The constants were determined at 15°, using the hydrogen chloride catalytic method, and the general procedure was similar to that already described (compare this vol., 318). In several cases the original concentration of the organic acid (a) was not determined before mixing, but a few minutes after the solutions of hydrogen chloride and organic acid had been mixed. It was thought that somewhat more concordant results might be obtained by this method, as the time occupied in mixing equal volumes of the two solutions is appreciable. At the end of the given time t, water was added to the contents of one of the bottles in order immediately to stop the esterification, and the mixture then titrated with standard barium hydroxide solution, using phenolphthalein as indicator.

We have investigated all the methylacrylic acids, with the exception of *iso*crotonic acid, and in addition we have determined the constants for the saturated analogues of these olefine acids if they were not already known.

The results are given in the table on p. 976.

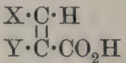
In connexion with these results, we desire to draw attention to the following points:

1. In previous papers attention has been drawn to the inhibiting action of the methyl group on esterification when introduced into the acetic acid molecule (Sudborough and Lloyd, Trans., 1899, **75**, 467), or into the molecule of methyl hydrogen succinate (Bone, Sudborough, and Sprankling, Trans., 1904, **85**, 534). The present results show, in quite as marked a manner, the inhibiting effect of methyl groups on esterification when introduced into the acrylic acid molecule. Thus the constant for acrylic acid is 3·09, and the value continues to fall for the various mono- and di-methylacrylic acids, until, in the case of trimethylacrylic acid, it has reached the value 0·0424, a value which is of somewhat the same order of magnitude as that for the acid ester, $CO_2Me\cdot CMe_2\cdot CH_2\cdot CO_2H$ (Trans., 1904, **85**, 540), or for α-chloro*allo*cinnamic acid (Trans., 1905, **87**, 1843).

Acid.	Series.	No. of titrations.	Conc. of hydrogen chloride.	$1/t \log_{10} a/a-x$. Min.	$1/t \log_{10} a/a-x$. Max.	Mean corrected for N-HCl.	$E^{15°}_{MeOH}$.
Unsaturated—							
Acrylic	*a* ...	4	0·04897*N*	0·0621	0·0695	1·34	3·09
	b ...	4	0·05862*N*	0·0746	0·0866	1·34	
Crotonic...	*a* ...	4	0·0852*N*	0·0452	0·0478	0·548	1·26
α-Methylacrylic	*a* ...	5	0·1116*N*	0·0380	0·0385	0·358	0·842
	b ...	4	0·08361*N*	0·0310	0·0317	0·373	
Tiglic	*a* ...	4	0·0670*N*	0·0120	0·0121	0·181	0·408
	b ..	4	0·0565*N*	0·0098	0·0100	0·176	
	c ...	6	0·0617*N*	0·0105	0·0111	0·174	
ββ-Dimethylacrylic.	*a* ...	4	0·1125*N*	0·0135	0·0143	0·123	0·285
	b ...	4	0·1522*N*	0·0181	0·0199	0·123	
	c ...	4	0·04411*N*	0·00534	0·00584	0·125	
	d ...	4	0·03224*N*	0·00391	0·00405	0·124	
Angelic	*a* ...	4	0·0532*N*	0·00260	0·00278	0·0508	0·116
	b ...	4	0·07385*N*	0·00401	0·00419	0·0552	
	c ...	4	0·0550*N*	0·00232	0·00309	0·0496	
Trimethylacrylic.	*a* ...	4	0·2012*N*	0·00367	0·00369	0·0183	0·0424
	b ...	4	0·1147*N*	0·00208	0·00218	0·0185	
Saturated—							
*iso*Butyric	*a* ...	4	0·00597*N*	0·0866	0·0882	14·7	33·6
	b ...	4	0·00940*N*	0·135	0·137	14·5	
α-Methylbutyric	*a* ...	4	0·02331*N*	0·120	0·136	5·46	12·6
	b ...	4	0·01782*N*	0·091	0·105	5·50	
	c ...	4	0·01787*N*	0·089	0·107	5·43	
*iso*Valeric	*a* ...	3	0 01057*N*	0·0568	0·0575	5·40	12·4
	b ...	4	0·04236*N*	0·216	0·226	5·25	
	c ...	3	0·04142*N*	0·216	0·229	5·37	
	d ...	4	0·03163*N*	0·170	0·178	5·50	
αβ-Dimethylbutyric.	*a* ...	5	0·0440*N*	0·0233	0·0255	0·547	1·25
	b ...	5	0·0450*N*	0·0228	0·0254	0·536	

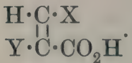
2. The results indicate in a most marked manner the great difference between the rates of esterification of an acrylic acid and of its substituted analogue, the presence of a double linking in the αβ-position always producing an enormous retardation in the esterification (compare table, this vol., p. 315).

3. Attention has been drawn previously (Trans., 1898, **73**, 93; 1905, **87**, 1842) to the different rates of esterification of two stereoisomeric acids of the types:



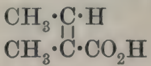
$$\begin{array}{c}X\cdot C\cdot H\\ \|\\ Y\cdot C\cdot CO_2H\end{array}$$

and



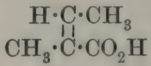
$$\begin{array}{c}H\cdot C\cdot X\\ \|\\ Y\cdot C\cdot CO_2H\end{array}.$$

When the substituent X is in the *cis*-position with respect to the carboxylic group, the acid is always esterified more slowly than when the substituent is in the *trans*-position. A comparison of the values for angelic and tiglic acids would indicate that tiglic acid is the *trans*- and angelic acid the *cis*-isomeride, as indicated in the formulæ:



$$\begin{array}{c}CH_3\cdot C\cdot H\\ \|\\ CH_3\cdot C\cdot CO_2H\end{array}$$

Tiglic acid.



$$\begin{array}{c}H\cdot C\cdot CH_3\\ \|\\ CH_3\cdot C\cdot CO_2H\end{array}$$

Angelic acid.

This supports the view put forward by Pfeiffer (*Zeitsch. physikal. Chem.*, 1904, **48**, 40).

4. Previous results (Trans., 1905, **87**, 1842) have shown that, as a rule, β-substituted acrylic acids are esterified more rapidly than their α-isomerides (compare also Anschütz, *Ber.*, 1897, **30**, 2652).

A comparison of the values for tiglic acid, 0·408, and ββ-dimethylacrylic acid, 0·285, at once shows that these acids are exceptional, as the ββ-dimethyl-substituted acid is esterified more slowly than an isomeric αβ-substituted acid. In connexion with this, it may be pointed out that the values for α-chlorocrotonic acid and β-chloro*iso*crotonic acid are practically identical, namely, 0·163 and 0·172 (Trans., 1905, **87**, 1843).

Notes on the Acids Used.

The acrylic acid was prepared by the removal of bromine from αβ-dibromopropionic acid as recommended by Biilmann (*J. pr. Chem.*, 1900, [ii], **61**, 215), and was obtained as a colourless liquid boiling at 70—71°/30 mm. It was not quite pure, and the results given in the table may be somewhat low. The α-methylacrylic acid was prepared by a method worked out several years ago in these laboratories by Dr. K. J. Thompson. One hundred and twenty-four grams of ethyl α-bromo*iso*butyrate and 100 grams of dimethylaniline are kept gently boiling in a flask provided with a long neck. At the end of each hour the fraction boiling below 125° is distilled over and collected. This consists mainly of ethyl α-methylacrylate, and after four hours the yield is about 35 grams. As the ester readily polymerises when heated, it is not advisable to purify it by repeated fractional distillation. The liquid boiling at 117—120° is hydrolysed by warming for several hours with alcoholic potash (1·5 mols.), and, on cooling, crystals of potassium α-methylacrylate separate in glistening plates. A further quantity can be obtained by evaporating the mother liquor, and the whole is purified by recrystallisation from hot alcohol. The pure salt is decomposed by a slight excess of 50 per cent. sulphuric acid and the acid extracted with pure ether; after drying the ethereal solution and removing the ether, the acid is obtained as a colourless oil, which sets to a crystalline mass when kept in the cold over phosphoric oxide. The melting point was 14·5°.

We have tried the method recommended by Lossen and Gerlach (*Annalen*, 1905, **342**, 112) for the preparation of α-methylacrylic acid, but the yields were always poor.

ββ-Dimethylacrylic acid was prepared by Barbier and Léser's method (*Bull. Soc. chim.*, 1905, [iii], **33**, 815) from mesityl oxide and sodium hypochlorite, and was purified by crystallisation from light petroleum (b. p. 50—60°), when it was obtained in brilliant, colourless prisms of considerable size and melting at 69°.

Both angelic and tiglic acids were crystallised from light petroleum (b. p. 35—40°); the former separated in small crystals, m. p. 45·5°, and the latter in extremely well-developed, water-clear crystals, m. p. 64·2°.

The trimethylacrylic acid was prepared from β-hydroxy-αβ-dimethyl-*n*-butyric acid (W. H. Perkin, Trans., 1896, **69**, 1482), the latter being obtained by Reformatsky's reaction from acetone, ethyl α-bromopropionate, and zinc. We have tried several methods with the object of obtaining a good yield of trimethylacrylic acid from this hydroxy-ester, but the yields in all cases were small.

The method of heating the acid with acetic anhydride and then boiling with aqueous potassium hydroxide gave 2·8 grams of trimethylacrylic acid from 10 grams of hydroxy-acid. The direct product of the action of acetic anhydride was not a free acid, as it did not dissolve in sodium carbonate solution, and it had no definite boiling point.

By carefully warming the ester of the hydroxy-acid with phosphoryl chloride, and then hydrolysing the product (b. p. 168—174°) with alcoholic potash, a yield of 2·1 grams of trimethylacrylic acid was obtained from 10 grams of the hydroxy-ester. The acid was crystallised from water, and obtained as colourless needles, m. p. 71°.

The *iso*butyric acid boiled at 154—154·5°/758 mm., the *iso*valeric acid at 176°/757 mm., and the α-methylbutyric acid at 174·5—176°/767 mm.

The αβ-dimethylbutyric acid was prepared by heating the corresponding malonic acid (Perkin, Trans., 1896, **69**, 1477), and, after three rectifications, was obtained as a colourless liquid boiling at 190—192°/767 mm.

We wish to thank the Research Fund Committee of the Chemical Society for a grant which has enabled us to defray part of the cost involved in this research.

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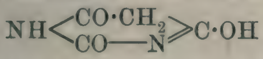
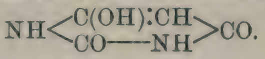
ABERYSTWYTH.

CXI.—*The Constitution of the Salts of Barbituric Acid.*

By JOHN KERFOOT WOOD and EMMA ALEXANDER ANDERSON.

IT has been shown by one of us (Wood, Trans., 1906, **89**, 1831), and also by Trübsbach (*Zeitsch. physikal. Chem.*, 1895, **16**, 711) and Hantzsch and Voegelen (*Ber.*, 1902, **35**, 1006), that barbituric acid is an acid considerably stronger than acetic acid. Such a value for the dissociation constant would be exceedingly high were the acidity to be due simply to the hydrogen of one of the imino-groups, but it was shown by Wood (*loc. cit.*) that most of the acidity was to be traced to the methylene group, the *C*-dialkylbarbituric acids having dissociation constants less than one-thousandth of that of the parent substance. Hantzsch and Voegelen (*loc. cit.*), from determinations of the electrical conductivity of solutions of barbituric acid in aqueous alcohol, had previously drawn the conclusion that barbituric acid is a pseudo-acid, but were unable to decide whether the acid, when in solution, had the formula  $\mathrm{NH}<\begin{matrix}\mathrm{CO\cdot CH_2}\\ \mathrm{CO{-}{-}N}\end{matrix}\geqslant\mathrm{C\cdot OH}$ or  $\mathrm{NH}<\begin{matrix}\mathrm{C(OH)\colon CH}\\ \mathrm{CO{-}{-}NH}\end{matrix}>\mathrm{CO}$. Taking the results obtained by Wood (*loc. cit.*) into account, and neglecting the slight acidity due to the imino-group, the second of these formulæ would be the correct one for the acid in solution, and the salts would have analogous formulæ, the hydrogen of the hydroxyl group being replaced by metals.

An alternative view to explain the high dissociation constant of barbituric acid would be that the ring might be broken by the action of water, giving rise to a ureido-acid,

$$\mathrm{NH_2\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot CO_2H},$$

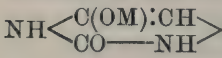
in the same way that parabanic acid is decomposed with the formation of oxaluric acid. Such a rupture of the ring is, however, very unlikely in the case of barbituric acid; rather would the ureido-acid containing a chain of six carbon and nitrogen atoms have a tendency to pass into barbituric acid, the conditions being favourable to ring formation. Further, it is exceedingly improbable that replacement of the hydrogens of the methylene group by alkyl groups would prevent the rupture of the ring, assuming it to take place in the case of barbituric acid, but some such effect would be necessary to account for the great discrepancy between the values of the dissociation constants of barbituric acid and its *C*-dialkyl derivatives. Finally, were rupture of the ring to take place, the salts of barbituric acid would be salts of the new ureido-acid, and on analysis would show a molecule of water more than would be the case were there no rupture. The fact that some of the salts are anhydrous and have compositions agreeing with the ring formula, shows that this alternative explanation is inadmissible.

From its intimate connexion with barbituric acid, it was considered that it would be of interest to prepare the above-mentioned ureidomalonic acid and to study its properties. Various attempts were made by the authors to prepare the compound by the hydrolysis of cyanoacetylcarbamide, but all of these, no matter what hydrolysing agent was used, were unsuccessful.

Attempts were then made to condense together malonic acid and carbamide, and from these substances, using acetic anhydride as the condensing agent, the amide of the desired acid was ultimately obtained. This amide, on treatment with sodium hydroxide, yielded a sodium salt, the composition of which agreed with that of sodium barbiturate, and, on being acidified, it yielded barbituric acid and not the ureido-acid. Such behaviour is in agreement with the observation of Boehringer and Söhne (D.R.-P. 193447), that the ethyl ester of ureidomalonic acid, on saponification, is converted into sodium barbiturate.

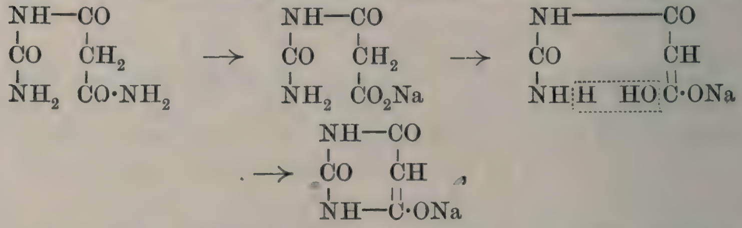
These results show that it is impossible to prepare and isolate the ureido-acid, since, owing to the tendency to ring-formation, it immediately loses water and passes into barbituric acid.

The formation of sodium barbiturate by the action of sodium hydroxide on the amide and ethyl ester of ureidomalonic acid shows conclusively that the salts of barbituric acid must have the constitution



$\mathrm{NH}\!<\!\begin{matrix}\mathrm{C(OM){:}CH}\\ \mathrm{CO{-\!-}NH}\end{matrix}\!>\!\mathrm{CO}$, where M represents a univalent metal.

This action of sodium hydroxide on the amide is shown as follows:



it being taken for granted that the nitrogen of the amido-group is removed, rather than that contained in the carbamide portion of the molecule.

EXPERIMENTAL.

Preliminary Experiments with Cyanoacetylcarbamide.—It has been shown by Traube (*Ber.*, 1900, 33, 1381) that cyanoacetylcarbamide, on treatment with sodium hydroxide, yields the sodium salt of 4-amino-2:6-dihydroxypyrimidine. In face of this result, alkalis appeared out of the question for the conversion of cyanoacetylcarbamide into ureidomalonic acid, but it was thought the cyanogen group might be hydrolysed by using some other agent. Hydrochloric acid was first tried, but without success, the only apparent result being to decompose the cyanoacetylcarbamide into cyanoacetic acid and carbamide. It was then attempted to hydrolyse the substance by heating it with water under pressure. Several grams were heated with water in a sealed tube to 120° for about eight hours. On opening the tube there was an escape of gas, and the liquid possessed a strong ammoniacal odour. A portion of the liquid, on treatment with hydrochloric acid, effervesced vigorously, owing to the escape of carbon dioxide. The liquid was at first slightly cloudy, but, on standing, a precipitate gradually formed. This was collected and dried; on analysis it proved to be 4-amino-2 : 6-dihydroxypyrimidine, its behaviour when dissolved in sodium hydroxide and treated with sodium nitrite and sulphuric acid supporting this conclusion. The liquid from which the pyrimidine had been precipitated was extracted with ether, and from the ethereal extract a small quantity of a solid acid was obtained; this substance possessed all the properties of cyanoacetic acid. It appears evident, therefore, that when cyanoacetylcarbamide is heated with water under pressure, part is converted into the isomeric 4-amino-2 : 6-dihydroxypyrimidine, whilst the rest is decomposed, forming eventually cyanoacetic acid, ammonia, and carbon dioxide, the latter two substances existing partly as ammonium carbonate. In view of these results no further attempts to prepare the ureido-acid from cyanoacetylcarbamide were made.

Attempts to Prepare Ureidomalonic Acid from Carbamide and Malonic Acid.

Grimaux (*Bull. Soc. chim.*, 1876, [ii], **31**, 146) first synthesised barbituric acid by the action of phosphoryl chloride on a mixture of carbamide and malonic acid. The authors considered that by using some other condensing agent it might be possible to attack only one of the carboxyl groups of the acid. A preliminary experiment was made in which a mixture of carbamide, malonic acid, and acetic anhydride, in equimolecular proportions, was heated on the water-bath. The mixture first melted, forming a clear yellow liquid, which soon burst into vigorous effervescence and deposited a yellow solid. When all apparent action was over, water was added to the mixture and the solid collected and dried. The percentage of nitrogen in the small amount of product obtained from this preliminary experiment suggested that the substance might possibly be malonylbiuret, and accordingly, in repeating the experiment on a larger scale, the proportions in which the original substances were mixed were such as would most favour the production of that compound, namely, two molecules each of carbamide and acetic anhydride and one molecule of malonic acid. This mixture, when heated on the water-bath, behaved as already described. On attempting to purify the product, it was found that it was not a single substance, as had been concluded from the preliminary experiment, but a mixture. The only liquid with any appreciable solvent action was water, and the mixture was accordingly submitted to fractional crystallisation from that liquid. The mixture was in this way resolved into three components, the most soluble of which was proved on analysis to consist of barbituric acid.

The third or least soluble component of the original product was a white powder, almost insoluble in boiling water, from which liquid it separated in fine needles:

0·1163 gave 0·1419 CO_2 and 0·0501 H_2O. C = 33·27; H = 4·78.
0·1147 „ 28·0 c.c. N_2 (moist) at 12·5° and 760 mm. N = 28·92.
$C_4H_7O_3N_3$ requires C = 33·10; H = 4·82; N = 28·96 per cent.

This result would agree with either ammonium barbiturate or the amide of ureidomalonic acid. From the fact that on grinding the substance in a mortar with soda-lime and a little water no ammonia was evolved, and that ammonia was only evolved very slowly on boiling the substance with a solution of sodium hydroxide, the former alternative appears to be impossible. It must be concluded, therefore, that one of the products formed by the action of acetic anhydride on a mixture of carbamide and malonic acid is the amide of ureidomalonic acid.

The amide, when dissolved in sodium hydroxide solution and then treated with sodium nitrite and dilute sulphuric acid, gave a deep magenta colour similar to that given by barbituric acid when treated in a similar manner.

Action of Sodium Hydroxide on Ureidomalonamide.—The compound on being boiled with a 2*N*-solution of sodium hydroxide wholly dissolved, and slowly evolved ammonia. No sodium salt separated from the liquid on cooling, but on the addition of alcohol a white precipitate, consisting of a sodium salt, was obtained. This was collected, washed with alcohol, and dried, first in the air and afterwards by heating to 120°:

0·2877 gave 0·1423 Na_2SO_4. Na = 16·02.
Sodium barbiturate requires Na = 15·33; sodium ureidomalonate requires Na = 13·6 per cent.

The sodium salt was dissolved in water and concentrated hydrochloric acid added. The solution, on keeping, deposited small crystals, which were collected, washed with water, and dried. The crystals melted and decomposed at 250—260°; a behaviour similar to that of barbituric acid :

0·1002 gave 19·3 c.c. N_2 (moist) at 11° and 742 mm. $N = 22·46$.
Barbituric acid requires $N = 21·87$; ureidomalonic acid requires $N = 19·19$ per cent.

It is evident, therefore, that ureidomalonamide is converted by sodium hydroxide into a salt of barbituric acid.

Examination of Second Fraction of Original Product.—This substance was less soluble than barbituric acid, but more soluble than the ureidomalonamide. It possessed a pale yellow colour, and readily evolved ammonia on treatment with a solution of sodium hydroxide. When dissolved in sodium hydroxide and mixed with sodium nitrite and sulphuric acid, no magenta colour was obtained, but a yellow, flocculent precipitate was produced when the sulphuric acid was added in excess; if the sodium nitrite were omitted, a similar precipitate was obtained when sulphuric acid was added to the alkaline solution :

0·1002 gave 0·1442 CO_2 and 0·0334 H_2O. $C = 39·24$; $H = 3·70$.
0·1035 ,, 19·2 c.c. N_2 (moist) at 11·5° and 765 mm. $N = 22·23$.

This result would agree fairly well with a substance having the formula $C_6H_7O_4N_3$, which requires $C = 38·91$, $H = 3·78$, $N = 22·70$ per cent. It being difficult to account for the formation of a compound having the above empirical formula, attempts were made to purify the substance by further treatment with boiling water. The results of analysis after this further treatment were slightly different from those given above, namely, $C = 39·33$, $H = 4·14$, $N = 21·77$; these results would point to the substance being much more complex than was indicated by the first analysis, the simplest formula with which they are in agreement being $C_{21}H_{26}O_{14}N_{10}$.

An attempt was made to determine the molecular weight of the compound by the ebullioscopic method, using water as solvent. The value obtained for the molecular weight was, however, only 61, and even allowing for the possibility of dissociation, this result was far too low to agree with any of the possible formulæ. It was noticed that the solutions obtained were never perfectly clear, but always more or less opalescent, and it was therefore thought possible that the solution formed was of a colloidal nature. If such were the case it would account for the result obtained in the molecular-weight determination, and this view was supported by the fact that on the addition of ammonium sulphate to the solution an immediate precipitate was obtained, similar in character to those given by solutions of proteins.

The substance formed by the addition of sulphuric acid to the alkaline solution of the original compound also appeared to be of a complex nature, the results of its analysis agreeing with an empirical formula of $C_9H_{13}O_9N_5$.

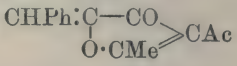
No suggestion as to the constitution of these substances can be given, as further experiments were rendered impossible by lack of material. It appears probable, however, that the substance composing the second fraction of the original product is a much more complex compound than those forming the other two fractions.

UNIVERSITY COLLEGE,
DUNDEE.

CXII.—*The Condensation of Amides with Esters of Acetylenic Acids.*

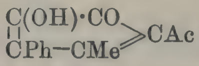
By SIEGFRIED RUHEMANN.

SOME years ago, it was shown (Ruhemann and Merriman, Trans., 1905, **87**, 1383) that phenylpropiolyl chloride reacts with sodioacetylacetone to form a yellow compound, $C_{14}H_{12}O_3$ (I), which has the remarkable property of changing under the influence of piperidine into a blue salt of a red isomeride (II), and that the latter on digestion with sodium carbonate is transformed into a colourless acid (III), isomeric with the other two substances. These compounds were represented thus:



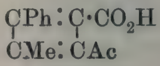
$$\begin{array}{l}\mathrm{CHPh{:}C{-}CO}\\ \qquad\quad\mathrm{O{\cdot}CMe}\end{array}\!>\!\mathrm{CAc}$$

(I.)



$$\begin{array}{l}\mathrm{C(OH){\cdot}CO}\\ \mathrm{CPh{-}CMe}\end{array}\!>\!\mathrm{CAc}$$

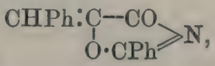
(II.)



$$\begin{array}{l}\mathrm{CPh{:}C{\cdot}CO_2H}\\ \mathrm{CMe{:}CAc}\end{array}$$

(III.)

With the view of preparing analogous heterocyclic substances containing nitrogen, I have treated phenylpropiolyl chloride with sodiobenzamide; but this reaction, instead of taking place in the manner similar to the formation of the furan derivative (I) and yielding phenylbenzylideneoxazolone,

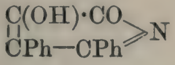


$$\begin{array}{l}\mathrm{CHPh{:}C{-}CO}\\ \qquad\quad\mathrm{O{\cdot}CPh}\end{array}\!>\!\mathrm{N},$$

furnishes diphenylpropiolylbenzamide, $(C_6H_5{\cdot}C{\vdots}C{\cdot}CO)_2N{\cdot}CO{\cdot}C_6H_5$. This result corresponds with the behaviour of benzoyl chloride towards sodiobenzamide, which, as Curtius (*Ber.*, 1890, **23**, 3040) showed, yields tribenzamide.

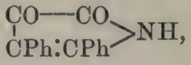
The interaction of ethyl phenylpropiolate and sodiobenzamide leads near to the desired end. This method has been used before (see

Curtius, *Ber.*, 1890, **23**, 3038; Titherley, Trans., 1902, **81**, 1520) for the formation of diacylimides, and has since been applied by Ruhemann and Priestley (Trans., 1909, **95**, 449) for the production of acyl derivatives of ethyl carbamate. The oxazolone compound, which, most probably, is first formed, cannot, however, be isolated, because, under the prevailing conditions, it suffers a transformation similar to the one which the furan derivative (I) undergoes to its red isomeride (II), and yields a deep red compound, $C_{16}H_{11}O_2N$. This is to be represented thus:



$$\begin{matrix} C(OH)\cdot CO \\ \| \\ CPh-CPh \end{matrix} > N$$

or



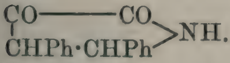
$$\begin{matrix} CO-CO \\ | \\ CPh:CPh \end{matrix} > NH,$$

and, therefore, to be called *diketodiphenylpyrroline.* Along with the cyclic compound, a colourless substance, $C_{23}H_{18}O_3N_2$, is produced, which undoubtedly owes its formation to the union of phenylpropiolylbenzamide with benzamide. It has, therefore, the constitution $C_6H_5\cdot C(NH\cdot CO\cdot C_6H_5):CH\cdot CO\cdot NH\cdot CO\cdot C_6H_5$, which characterises it as the *benzamide* of *β-benzoylaminocinnamic acid.*

The correctness of the view concerning the constitution of the compound, $C_{16}H_{11}O_2N$, follows from the fact that, on boiling with potassium hydroxide, it decomposes quantitatively, thus:

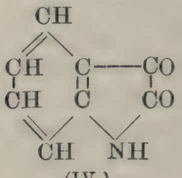
$$C_{16}H_{11}O_2N + 3H_2O = C_2H_2O_4 + NH_3 + C_6H_5\cdot CH_2\cdot CO\cdot C_6H_5,$$

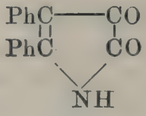
and furnishes deoxybenzoin, besides ammonia and oxalic acid. Diketodiphenylpyrroline dissolves in dilute alkalis to yield blue solutions, which, however, rapidly turn yellow; on adding dilute hydrochloric acid, the red pyrroline derivative is precipitated unchanged. This behaviour resembles that of isatin in forming violet solutions with alkalis, which change to yellow and then contain the salts of isatoic acid. Like isatin, diketodiphenylpyrroline forms a phenylhydrazone which is insoluble in alkalis or acids. As may be expected, both compounds differ in their behaviour towards reducing agents. Whereas isatin, on treatment of its solution in glacial acetic acid with zinc dust, yields isatide, $C_{16}H_{12}O_4N_2$, diketodiphenylpyrroline, under the same conditions, is reduced to *diketodiphenylpyrrolidine*

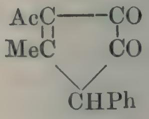


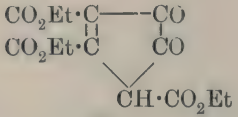
$$\begin{matrix} CO-CO \\ | \\ CHPh\cdot CHPh \end{matrix} > NH.$$

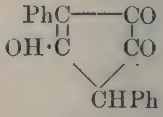
Diketodiphenylpyrroline (V) not only resembles isatin (IV), but also the red *cyclo*pentene derivative (VI), and this resemblance follows both from the similarity of their formation and from their property of yielding blue salts. This fact, in turn, supports the constitution of the latter substance. There can neither be any doubt as to the relation of these compounds with triethyloxalylaconitate (VII), which Ruhemann and Hemmy (Trans., 1897, **71**, 34) obtained from ethyl oxaloacetate, and to Claisen and Ewan's oxalyldibenzyl ketone (VIII) (*Annalen*, 1895, **284**, 245). The connexion between these substances finds its full expression in their formulæ:


(IV.)

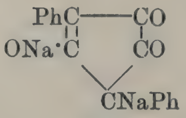

(V.)

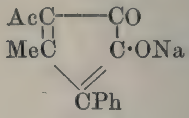

(VI.)

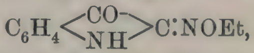
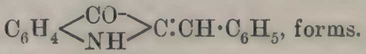

(VII.)

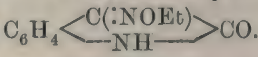
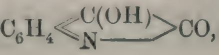

(VIII.)

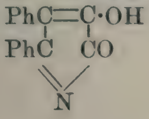
As to the constitution of the violet or blue salts which these compounds form, Claisen and Ewan (*loc. cit.*) expressed the view that the blue disodio-derivative of oxalyldibenzyl ketone is probably to be formulated as (IX), whereas Ruhemann and Merriman (*loc. cit.*) represented the blue salt of the *cyclo*pentene derivative (VI) by formula (X):

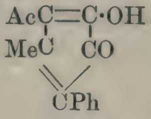

(IX.)

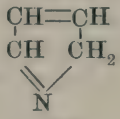

(X.)

The following considerations, however, lead to the conclusion that neither view is correct. Von Baeyer, in the course of his classical researches on the indigo group, showed that the ethyl ether of ψ-isatin-α-oxime,  $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{NH}>C:NOEt$, with sodium hydroxide yields a blue salt similar to the one which the indogenide of benzaldehyde,  $C_6H_4<\genfrac{}{}{0pt}{}{CO-}{NH}>C:CH\cdot C_6H_5$, forms. It follows, therefore, that the replacement of the oxygen of the α-ketonic group in ψ-isatin by a bivalent group does not interfere with the formation of a blue salt.

The result is different, however, if the oxygen of the β-ketonic group of ψ-isatin is substituted by such a group, as in the ethyl ether of isatoxime,  $C_6H_4<\genfrac{}{}{0pt}{}{C(:NOEt)}{NH}>CO$. In this case, a blue salt is not formed. This result indicates that the metal is not attached to the nitrogen of the imino-group, as von Baeyer suggests, but to the oxygen of the β-ketonic group. It follows, therefore, that isatin in its violet salts appears in its tautomeric form,  $C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{N}>CO$, and this grouping will be found in the salts of those derivatives in which the oxygen of the α-ketonic group is replaced by bivalent radicles. In this form isatin appears as an orthoquinone derivative. Owing to the similarity which exists between isatin and the above-mentioned compounds, the view is justified that their salts have an analogous constitution; for instance, corresponding with (V) and (VI):


(V*a*.)


(VI*a*.)


(XI).

It may be mentioned that in the case of pyrrole, previous investigators have been obliged to consider the possibility of its existing in a tautomeric form, for pentachloropyrrole is undoubtedly derived from the tautomeride (XI), which, according to the above remarks, would exist, also, in the salts of diketodiphenylpyrroline.*

The reaction of ethyl phenylpropiolate with sodiobenzamide seems to be typical of the behaviour of the sodium derivatives of aromatic amides with the esters of acetylenic acids. This would follow from the fact that sodio-*o*-toluamide yields diketophenyl-*o*-tolylpyrroline,

$$C_{17}H_{13}O_2N,$$

which closely resembles its lower homologue. The sodium derivatives of fatty or fatty-aromatic amides, however, do not condense with ethyl phenylpropiolate to cyclic substances, instead diacylimides are formed, as phenylpropiolylphenylacetamide,

$$C_6H_5\cdot C\vdots C\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot C_6H_5,$$

from the acetylenic ester and sodiophenylacetamide.

EXPERIMENTAL.

Diphenylpropiolylbenzamide, $(C_6H_5\cdot C\vdots C\cdot CO)_2N\cdot CO\cdot C_6H_5$.

As stated in the introduction, this compound is formed by the action of phenylpropiolyl chloride on sodiobenzamide. The latter substance was prepared according to Blacher's method (*Ber.*, 1895, **28**, 432) by evaporating the absolute alcoholic solution of the mixture of sodium ethoxide and benzamide in a vacuum, first from the water-

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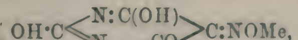
* The relation which exists between the above-named substances may be extended to other classes of compounds which, like violuric acid, form coloured salts. Their structure:



$$OH\cdot C\genfrac{<}{}{0pt}{}{N:C(OH)}{N\text{——}CO}>C:NOMe,$$

indicates a certain resemblance to the constitution of the metallic derivatives of diketodiphenylpyrroline and its analogues; for it also has an orthoquinone grouping and the same relative position of the metal in the molecules of the salts (see also Hantzsch and Isherwood, *Ber.*, 1909, **42**, 986).

bath and finally from the oil-bath, which is gradually heated to 200°. On adding phenylpropiolyl chloride (8·2 grams) to the dry sodiobenzamide (7·1 grams), suspended in benzene, heat is developed. The mixture, after being kept for a short time at the ordinary temperature, is digested on the water-bath for about half an hour, the benzene is evaporated, and the dark-coloured residue washed with ether, when a faintly-coloured solid remains undissolved. This is soluble in a large amount of boiling alcohol, and, on cooling, separates in almost colourless needles melting at 242°:

0·1955 gave 0·5692 CO_2 and 0·0745 H_2O. C = 79·40 ; H = 4·23.
0·2082 ,, 7 c.c. N_2 at 19° and 743 mm. N = 3·78.
$C_{25}H_{15}O_3N$ requires C = 79·57 ; H = 3·98 ; N = 3·71 per cent.

Action of Sodiobenzamide on Ethyl Phenylpropiolate.

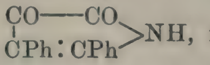
On mixing finely-powdered sodiobenzamide (7·1 grams), suspended in dry benzene, with ethyl phenylpropiolate (8·7 grams), no visible change takes place at the ordinary temperature, but an action sets in, which is indicated by the development of a deep blue coloration, if the mixture is heated on the water-bath for a short time. After an hour's digestion, the benzene is evaporated, and the residue treated with water, when the blue colour disappears. The whole is then agitated with ether, which extracts small quantities of unaltered benzamide and ethyl phenylpropiolate, and the aqueous layer is mixed with an excess of dilute hydrochloric acid. An oil separates which, on removal of the dissolved ether, sets to a solid. This is a mixture of the deep red diketodiphenylpyrroline and the colourless benzamide of β-benzoylaminocinnamic acid. These compounds differ but slightly in the degree of solubility in organic solvents ; they dissolve, also, in dilute potassium hydroxide or sodium carbonate ; their separation, therefore, presented great difficulties until it was found that, on saturating the alkaline solutions of the mixture with carbon dioxide, the colourless compound is precipitated, but not the coloured diketodiphenylpyrroline.

The Benzamide of β-Benzoylaminocinnamic Acid,

$$C_6H_5\cdot C(NH\cdot CO\cdot C_6H_5)\colon CH\cdot CO\cdot NH\cdot CO\cdot C_6H_5,$$

separates, on passing carbon dioxide through the solution of the product of the reaction in dilute potassium hydroxide, as a light red solid, which, when washed with a little dilute alcohol, becomes colourless. It is insoluble in water, but readily dissolves in glacial acetic acid, ethyl acetate, ether, or hot alcohol, and, on cooling its solution in boiling dilute alcohol, crystallises in needles, which melt at 188° to a red liquid:

0·1950 gave 0·5370 CO_2 and 0·0890 H_2O. C = 75·10 ; H = 5·07.
0·1840 ,, 12·4 c.c. N_2 at 18° and 748 mm. N = 7·65.
$C_{23}H_{18}O_3N_2$ requires C = 75·13 ; H = 4·86 ; N = 7·57 per cent.

Diketodiphenylpyrroline,  $\begin{matrix}\mathrm{CO{-}{-}CO}\\ \mathrm{CPh:CPh}\end{matrix}\!>\!\mathrm{NH}$, is contained in the pale yellow filtrate from the former compound. On adding dilute hydrochloric acid, a faintly-coloured emulsion is first produced, which is shortly transformed into a red solid. This is scarcely soluble in boiling water, but just sufficiently to yield a red solution ; it is readily soluble in ether, acetone, or alcohol, and, on cooling its concentrated solution in hot alcohol, separates in beautiful, deep red needles, which melt and decompose at 184° :

0·1960 gave 0·5537 CO_2 and 0·0820 H_2O. C = 77·04 ; H = 4·64.
0·2452 ,, 12 c.c. N_2 at 20° and 764 mm. N = 5·62.
$C_{16}H_{11}O_2N$ requires C = 77·11 ; H = 4·42 ; N = 5·62 per cent.

Diketodiphenylpyrroline dissolves in dilute potassium hydroxide to yield a deep blue solution, which rapidly turns yellow ; this, no doubt, contains the salt of aminostilbeneoxalic acid,

$$NH_2\cdot CPh{:}CPh\cdot CO\cdot CO_2H,$$

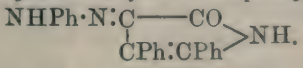
for, on adding dilute hydrochloric acid, a faintly-coloured emulsion is first produced, which, however, readily loses water and condenses to diketodiphenylpyrroline. This reaction, therefore, resembles the behaviour of alkalis towards isatin.

On boiling diketodiphenylpyrroline with an excess of dilute potassium hydroxide, it is decomposed and yields ammonia, oxalic acid, and deoxybenzoin. The heating is continued until the evolution of ammonia ceases ; the deoxybenzoin which separates is collected and recrystallised from dilute alcohol, when it is obtained in colourless needles, which are volatile with steam and melt at 60° :

0·1657 gave 0·5200 CO_2 and 0·0925 H_2O. C = 85·59 ; H = 6·20
$C_{14}H_{12}O$ requires C = 85·71 ; H = 6·12 per cent.

The yield of deoxybenzoin amounts to 90 per cent. of the theoretical. The alkaline filtrate from this product of the decomposition of diketodiphenylpyrroline contains oxalic acid, which was isolated in the form of its calcium salt.

The Phenylhydrazone of Diketodiphenylpyrroline,



$$\begin{matrix}\mathrm{NHPh\cdot N{:}C{-}{-}CO}\\ \mathrm{CPh{:}CPh}\end{matrix}\!>\!\mathrm{NH}.$$

Like isatin, diketodiphenylpyrroline readily forms a phenylhydrazone if its alcoholic solution is boiled with phenylhydrazine on the water-bath. It separates from the hot solution as a red, crystalline solid, which is soluble in hot benzene; it is almost insoluble in cold alcohol, but it dissolves in a large volume of boiling alcohol, and, on cooling, crystallises in vermilion needles, which melt and decompose at 231°:

0·1827 gave 19·8 c.c. N_2 at 19° and 759 mm. N = 12·43.

$C_{22}H_{17}ON_3$ requires N = 12·36 per cent.

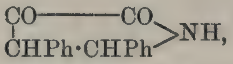
Reduction of Diketodiphenylpyrroline.

On adding zinc dust to the hot solution of diketodiphenylpyrroline in glacial acetic acid, the red colour is quickly discharged, and the colourless filtrate yields a white precipitate on the addition of water. This is fairly soluble in hot dilute alcohol, and, on cooling, crystallises in faintly-yellow needles, which turn brown at about 165°, and at 233—234° melt to a dark liquid:

0·1907 gave 0·5338 CO_2 and 0·0905 H_2O. C = 76·34; H = 5·27.
0·2072 „ 10·4 c.c. N_2 at 19° and 744 mm. N = 5·64.

$C_{16}H_{13}O_2N$ requires C = 76·49; H = 5·18; N = 5·58 per cent.

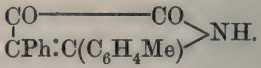
The compound, which most probably is to be regarded as diketodiphenylpyrrolidine,



$$\left.\begin{array}{l}\mathrm{CO}\text{———}\mathrm{CO}\\ \mathrm{CHPh{\cdot}CHPh}\end{array}\right>\mathrm{NH},$$

yields a deep bluish-green coloration on the addition of ferric chloride to its alcoholic solution.

Diketophenyl-o-tolylpyrroline,



$$\left.\begin{array}{l}\mathrm{CO}\text{————}\mathrm{CO}\\ \mathrm{CPh{:}C(C_6H_4Me)}\end{array}\right>\mathrm{NH}.$$

Sodio-*o*-toluamide behaves similarly to sodiobenzamide in its action on ethyl phenylpropiolate. The reaction in this case was carried out as follows. *o*-Toluamide (6·5 grams) is dissolved in absolute ether (of which a large quantity is required, as the amide is but sparingly soluble in this solvent), and the solution digested with sodium wire (1·1 gram) on the water-bath. In the course of a day the metal disappears; ethyl phenylpropiolate (8·4 grams) is then added, and the digestion continued. The mixture shortly turns blue; after about an hour the ether is evaporated, and, in order to complete the reaction, the residue is mixed with dry benzene and digested for a short time.

The benzene is finally distilled from the water-bath and water added to the product, when the blue colour disappears. After removal of the unaltered toluamide and ethyl phenylpropiolate by extraction with ether, an excess of dilute hydrochloric acid is added to the aqueous layer, which precipitates a dark red substance. This is dissolved in cold dilute potassium hydroxide, and the solution saturated with carbon dioxide. As in the case of the same treatment of the product which is formed from sodiobenzamide and ethyl phenylpropiolate, a yellowish-red solid is precipitated. I have not examined it, but there cannot be any doubt that it has the formula,

$$C_6H_5\cdot C(NH\cdot CO\cdot C_6H_4\cdot \overset{(o)}{C}H_3){:}CH\cdot CO\cdot NH\cdot CO\cdot C_6H_4\cdot \overset{(o)}{C}H_3.$$

The pale yellow filtrate from this substance, on the addition of dilute hydrochloric acid, yields a red compound, *diketophenyl-*o*-tolylpyrroline*, which is readily soluble in ether or alcohol and crystallises from its concentrated alcoholic solution in beautiful deep red prisms melting at 165—166°:

0·1919 gave 0·5445 CO_2 and 0·0860 H_2O. C = 77·38; H = 4·95.
0·2140 ,, 10·2 c.c. N_2 at 19° and 757 mm. N = 5·45.
$C_{17}H_{13}O_2N$ requires C = 77·57; H = 4·94; N = 5·32 per cent.

This substance closely resembles diketodiphenylpyrroline; it dissolves in dilute potassium hydroxide, yielding a blue solution which rapidly turns yellow. With phenylhydrazine it forms the *phenylhydrazone*, $C_{17}H_{13}ON{:}N\cdot NH\cdot C_6H_5$, which separates in red crystals if the alcoholic solution of the pyrroline is digested with phenylhydrazine on the water-bath for one to two hours and then cooled. It is sparingly soluble in cold, moderately so in boiling, alcohol, and, on cooling, crystallises in scarlet prisms, which melt at 201—202°:

0·2068 gave 21·6 c.c. N_2 at 19° and 753 mm. N = 11·89.
$C_{23}H_{19}ON_3$ requires N = 11·90 per cent.

Action of Ethyl Phenylpropiolate on the Sodium Derivatives of Fatty and Fatty-aromatic Amides.

I have mentioned before (p. 987) that this reaction differs from that which occurs in the condensation of the acetylenic ester with the sodium compounds of aromatic amides, inasmuch as condensation to pyrroline derivatives does not take place, but diacylimides are produced.

Phenylpropiolylphenylacetamide, $C_6H_5\cdot C{\vdots}C\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot C_6H_5$.

Sodiophenylacetamide was prepared by Blacher's method (*loc. cit.*), by evaporating the alcoholic solution of the mixture of phenylacetamide and sodium ethoxide in a vacuum, first on a water-bath and then up to 200° on an oil-bath. To the powdered sodium compound (8 grams), suspended in dry benzene, ethyl phenylpropiolate (8·7 grams) is added, and the mixture boiled on the water-bath for an hour. The benzene is evaporated, and the brown, viscous residue treated with water and ether, when the whole dissolves. After removal of the ethereal layer, dilute hydrochloric acid is added to the dark aqueous solution, when a yellow oil is precipitated which partly sets to a solid. This is washed with cold alcohol and dissolved in boiling alcohol; from the concentrated solution, on cooling, yellow prisms separate, which melt at 209—210°:

0·1848 gave 0·5255 CO_2 and 0·0847 H_2O. C = 77·55; H = 5·09.
0·2245 ,, 10·8 c.c. N_2 at 20° and 758 mm. N = 5·48.
$C_{17}H_{13}O_2N$ requires C = 77·57; H = 4·94; N = 5·32 per cent.

I have ascertained, also, that sodioacetamide, when suspended in dry ether or benzene and digested with ethyl phenylpropiolate, does not yield a coloured compound which has properties similar to diketodiphenylpyrroline, but forms an almost colourless substance which is sparingly soluble in alcohol. This I have not further examined, but there cannot be any doubt that it is phenylpropiolylacetamide.

I am engaged in the continuation of the study of the pyrroline derivatives described above, and also in the investigation of the action of amides on esters of other acetylenic acids.

University Chemical Laboratory,
Cambridge.

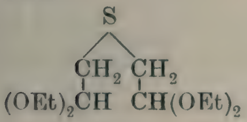
CXIII.—*Diethoxythioxan; a Relation between the Refractive Power and Chemical Activity of some Sulphur Compounds.*

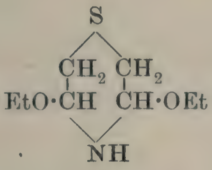
By Hans Thacher Clarke and Samuel Smiles.

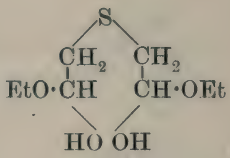
The experiments described in this paper were originally undertaken with the intention of examining thiazine, the parent substance of the dibenzothiazine derivatives which have been recently studied by one of the present authors and T. P. Hilditch (Trans., 1908, **93**, 145, 1687). So far as this object is concerned, the results have not yet been successful; in fact, our progress along the lines of investigation which we originally planned has been barred by the unexpected stability of one of the intermediate products. The latter substance, which is a saturated cyclic sulphide, seemed of interest on account of the comparatively inert state of the bivalent sulphur atom contained in it, and we therefore examined more closely the chemical activity of the compound. The results of this investigation are described in the following pages, and finally we offer what appears to us to be the only rational explanation of the anomaly.

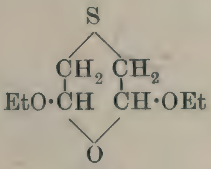
By the interaction of sodium sulphide and chloroacetal, the acetal sulphide (I) is formed in the usual manner, and it was hoped that by the action of ammonia on this, under suitable conditions, the imino-group might be introduced, forming the thiomorpholine derivative (II). Acetal sulphide, however, seems very stable towards alkaline reagents, and experiments in this direction have not led to the desired result.

On the other hand, acetal sulphide is immediately attacked by cold mineral acids, as indeed might be expected from the presence of the acetal grouping. But in these reactions the aldehyde which we hoped easily to convert to the required nitrogen derivative is not formed, the product being the cyclic compound * (IV), which no doubt is produced by elimination of water from the alcoholate (III).


(I.)


(II.)


(III.)


(IV.)

So far as we are aware, the only other derivatives of thioxan which have been met with are the so-called diethylene oxide sulphone, which Baumann and Walter (*Ber.*, 1893, **26**, 1138) obtained by the action of barium hydroxide on diethylene disulphone and the anhydride of thiodiglycollic acid (Anschütz and Biernaux, *Annalen*, 1893, **273**, 68); but these substances were not very fully investigated. The diethoxythioxan which we have obtained in the previously described manner is worth especial notice on account of its well-defined physical properties, its general stability, and the depressed reactivity of the sulphur in comparison with that of the corresponding open-chain compound. We have paid especial attention to the last-named property.

The open-chain compound, acetal sulphide, shows all the usual properties of a substance in which bivalent sulphur is united to saturated hydrocarbon groups; for example, it furnishes additive products with mercuric chloride and iodide, it is oxidised by hydrogen dioxide at the atmospheric temperature to a sulphoxide, and, under certain conditions, it combines readily with alkyl iodides. On the other hand, diethoxythioxan neither combines with mercuric halides nor reacts with hydrogen dioxide under the conditions chosen for comparison, and even in the presence of mercuric iodide the addition of alkyl iodide proceeds extremely slowly.

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* Structures such as that of the monoaldehyde and others cannot be entertained, since the substance is devoid of the usual reducing properties of aldehydes and α-ketols, and does not yield a hydrazone or acyl derivatives.

These comparative data are summarised in the following table, and, in order to show the normal character of acetal sulphide, the reactions of another sulphide of high molecular weight are inserted. Dibenzyl sulphide is chosen for this latter comparison:

	Result with		
Reagent.	Dibenzyl sulphide.	Acetal sulphide.	Diethoxythioxan.
$HgCl_2$ or HgI_2 and acetone or alcoholic solution.	Immediate formation of $(CH_2Ph)_2S{\cdot}HgX_2$ (Trans., 1900, **77**, 165).	Immediate formation of $[(EtO)_2CH{\cdot}CH_2]_2S{\cdot}HgX_2$	No reaction detected.
H_2O_2 (excess) in acetone solution for three days at ordinary temperature.	Almost quantitative formation of $(CH_2Ph)_2SO$ (Gazdar & Smiles, Trans., 1908, **93**, 1833).	Sulphoxide formed, apparently quantitative.	Almost all the original compound was isolated unaltered.
Excess of ethyl iodide and one molecular proportion of HgI_2 at the atmospheric temperature.	Formation of $(CH_2Ph)_2SEtI,HgI_2$ complete in five hours (Hilditch & Smiles, Trans., 1907, **91**, 1393).	Good yield of sulphonium salt obtained in five hours.	After eight hours, no sulphonium salt could be detected, and after 24 hours, only a small amount.

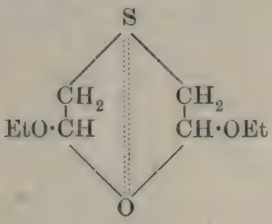
The results of the last-named reaction are the most interesting. It has been shown elsewhere (Smiles, Trans., 1900, **77**, 163; Hilditch and Smiles, Trans., 1907, **91**, 1393) that the addition of mercuric halide to a mixture of alkyl halide and sulphide enormously accelerates the formation of the sulphonium salt; in fact, it has been shown that the union of ethyl iodide and dimethyl sulphide, which in ordinary circumstances is scarcely complete in three days, may be effected in about fifteen minutes if mercuric iodide be present. At one time or another, one of the present authors has examined about fifteen of these reactions with saturated sulphides, and the thioxan derivative now described stands out as by far the most sluggish of all of them.

In attempting to find some explanation of the comparative inactivity of the sulphur in this substance, it is natural to turn first to the hypothesis of steric hindrance, since this has usually been employed to account for the depressed activity of a group.

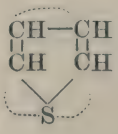
But it is evident that the usual theories do not apply in this case, for the only substituents in the thioxan system are not adjacent to the sulphur atom. Moreover, to assume that the thioxan ring is so distorted as to prevent the addition of groups to the sulphur atom appears to us to be quite unjustifiable, although it must be admitted that little is yet known of the steric conditions of heterocyclic systems. For these reasons, we consider that steric hindrance cannot be applied to explain the anomalous behaviour of this substance. But a satisfactory explanation is furnished by considerations similar to those employed by Thiele (*Annalen*, 1899, **306**, 87; **308**, 333) in accounting for the inert state of the central carbon atoms of a conjugated system of two ethenoid linkings. It is well known that here the partial valencies or residual affinities of these carbon atoms are supposed to satisfy each other, so that additive reagents are not taken up at this point, but at the first and fourth carbon atoms of the chain.

That the bivalent sulphur in saturated hydrocarbon sulphides is endowed with residual affinity has been evident since the earliest researches on these compounds, when their additive reactions were discovered, and since the work of Collie and Tickle on dimethylpyrone (Trans., 1899, **75**, 710) and of Friedel on dimethyl ether (*Bull. Soc. chim.*, 1875, [ii], **24**, 160, 241), the same has been admitted for bivalent oxygen.

Making this assumption of the unsaturated nature of the sulphur and oxygen—and it scarcely can be disputed—we advance as an explanation of the inactivity of the sulphur the hypothesis that the residual affinities of these elements partially saturate one another, and since the usual formulæ are insufficient to represent this state, we suggest that this thioxan derivative should be represented as follows (V):



(V.)



(VI.)

If the justice of hypotheses such as that put forward by Thiele be admitted, the only objection which can be raised against the present scheme is that the elements the residual affinities of which are combined are in the 1:4-positions of a six-membered ring instead of being adjacent. But this difficulty is readily overcome when it is remembered that much evidence has already been collected to show that unsaturated atoms in this 1 : 4-position of a six-membered ring system are peculiarly liable to influence one another, and in some cases combination by means of the usual valencies has been observed. In fact, in the light of this evidence, it appears probable that some connexion between unsaturated atoms in this position should exist. In the case of homocyclic compounds, it is sufficient to recall the researches of Collie (Trans., 1897, **71**, 1013) and of Baly, Edwards, and Stewart (Trans., 1906, **89**, 514) on the mobility of the benzene system. The latter-named investigators showed (*loc. cit.*, p. 525) that at a certain phase in the pulsation of the system the residual affinities of the 1 : 4-atoms will temporarily saturate each other, and this afforded an explanation of the previously observed tautomerism of phenol (Baly and Ewbank, Trans., 1905, **85**, 1348); also there is spectroscopic evidence to show (Stewart, *Stereochemistry*, 1907, p. 486) that the carbonyl groups in *cyclo*hexan-1 : 4-dione influence each other in such a way as to cause abnormal reactivity. With regard to heterocyclic systems, it may be observed that Dewar (*Zeitsch. Chem.*, 1871, **7**, 117) and Riedel (*Ber.*, 1883, **16**, 1609) entertained the idea that the nitrogen and γ-carbon atoms of the pyridine nucleus are united; further, that the usually accepted formula for acridine shows the union between the nitrogen and *meso*-carbon atom, and that the alternative formula for pyrazine and its derivatives shows a similar union between the nitrogen atoms. Finally, it may be mentioned that the recent work of Collie on dimethylpyrone has shown that a close relation exists between the carbonyl group and the cyclic oxygen.

The thioxan derivative which we have examined is not the only bivalent sulphur compound of abnormal properties. The case of thiophen is of particular interest in the present discussion, since, like thioxan, it contains other unsaturated atoms besides sulphur. The attempts made by Victor Meyer and his pupils (*Die Thiophengruppe*, Braunschweig, 1888) to combine this substance with alkyl iodides were unsuccessful, and oxidation experiments to obtain the sulphone met with similar results. In fact, the sulphur in thiophen closely resembles in chemical character that of diethoxythioxan, and similar considerations give a satisfactory explanation of its inactivity. So far as the state of the sulphur is concerned, the thiophen molecule is well represented by some formula, such as that written above (VI), which shows the residual affinity of that element to be partly saturated by that of the adjacent carbon atoms. Other examples of compounds containing sulphur of subnormal activity are the aromatic sulphides, and these also contain unsaturated groups adjacent to the sulphur.

We have also examined the refractive power of diethoxythioxan and the other sulphur compounds previously mentioned, and the evidence thus obtained supports the conclusions made from the chemical behaviour of the substance. Brühl has concluded (*Ber.*, 1907, **40**, 878, 1153), from a general survey of the refractivities of unsaturated compounds, that the refractive power of these substances is abnormal if the unsaturated groups are adjacent, or, using the term introduced by Thiele, if these groups are conjugated. Brühl seems to have applied the term conjugated to any system of unsaturated atoms or groups the residual affinities of which exert a mutual influence; and in this sense, which we consider desirable, the application of the term is wider than that originally made by Thiele. It may be mentioned that Brühl has drawn attention (*loc. cit.*, p. 1154) to a few exceptions to his rule, nevertheless optical anomaly has been generally accepted by chemists as an excellent supplement to chemical evidence in detecting the presence of "conjugated" atomic groupings.

The relations discovered by Brühl with carbon, nitrogen, and oxygen compounds hold also with sulphur compounds in which unsaturated atoms are adjacent to this element. Indeed, Brühl has already drawn attention to the behaviour of thiophen, which shows a remarkable depression in molecular refractive power:

Thiophen.	M_α (obs.).	M_α (calc.).	Δ.
C_4H_4S …………	24·14	25·40	1·26

Also diphenyl sulphide, which reacts sluggishly with alkyl iodides (Schöller, *Ber.*, 1874, **7**, 1274) and mercuric halides, shows optical anomaly. The refractive index of this substance was determined by Gladstone (*Journ. Chem. Soc.*, 1870, **23**, 147):

	M_α (obs.).	M_α (calc.).	Δ.
Diphenyl sulphide, $C_6H_5 \cdot S \cdot C_6H_5$…		$2 \times C_6H_6$ = 51·86	
		Less 2H = 2·20	
		49·66	
		S as in Et_2S = 8·00	
	58·97	57·66	+ 1·31

Another aromatic sulphide may be added as a further example:

	M_α (obs.).	M_α (calc.).	Δ.
Dihydroxydiphenyl sulphide, $S(C_6H_4 \cdot OH)_2$		$2 \times C_6H_4 \cdot OH$ = 55·50	
		Less 2H = 2·20	
		53·30	
		S as in Et_2S = 8·00	
	65·16	61·30	+ 3·86

The refractivity of diallyl sulphide has been measured by Nasini and Scala (*Gazzetta*, 1887, **17**, 76):

	M_α (obs.).	M_α (calc.).	Δ.
Diallyl sulphide, $(C_3H_5)_2S$...	36·73	Sum of atomic * refractivities = 36·79	− 0·06

The data show this compound to be normal, and since there is no direct chemical proof whether it has the structure:

$$(CH_2\colon CH\cdot CH_2)_2S \text{ or } (CH_3\cdot CH\colon CH)_2S,$$

the former alternative may be adopted as conforming to the optical evidence. As bearing on this question, it may be mentioned that Eykman has deduced from refractivity data (*Chem. Weekblad*, 1906, **3**, 711) that allyl cyanide has the structure: $CH_2\colon CH\cdot CH_2\cdot CN$. In correspondence with the normal refractive power of allyl sulphide, the reactivity of the sulphur is normal, for Semmler (*Annalen*, 1887, **241**, 118) has obtained a mercuric chloride additive product, and diallylsulphonium salts have been prepared (Cahours, *Zeitsch. Chem.*, 1865, 438; and Bayer and Co., 1898, D.R.-P. 97207).

Turning now to the thioxan derivative and the substances of normal reactivity with which it is compared in the table, it is found that the latter compounds are optically normal, whilst diethoxythioxan is slightly abnormal:

	M_α (obs.).	M_α (calc.).	Δ.
Dibenzyl sulphide, $(C_6H_5\cdot CH_2)_2S$		$2 \times C_6H_4Me$ = 61·58	
		Less 2H = 2·20	
		59·38	
		S as in Et_2S = 8·00	
	67·42	67·38	+ 0·04

The contrast between this normal sulphide and phenyl sulphide is worth special mention. In the latter substance, the bivalent sulphur atom is directly united with the unsaturated carbon atoms of the benzene nuclei, the reactivity and refractive power are consequently abnormal; but in the normal benzyl sulphide the sulphur is isolated from each benzene nucleus by an intervening saturated group.

In calculating the refractivity of acetal sulphide, the value found by Brühl (*Zeitsch. physikal. Chem.*, 1891, **7**, 160) for acetal has been employed.

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* In all these calculations, the atomic refractivity of sulphur employed is that deduced from Nasini's measurement (*Ber.*, 1882, **15**, 2878) of the refractive power of diethyl sulphide. The reactivity of this substance is normal. The values quoted for dibenzyl sulphide and dihydroxydiphenyl sulphide are those observed by Nasini and are taken from his article on the subject in *Nuova Enciclopedia di Chimica*, I, 792 (1906).

	M_α (obs.).	M_α (calc.).	Δ.
Acetal sulphide, $C_{12}H_{26}O_4S$……		2 × acetal = 65·76	
		Less 2H = 2·20	
		63·56	
		S as in Et_2S = 8·00	
	71·61	71·56	+ 0·05

Here again the refractive power and chemical activity are normal.

	M_α (obs.).	M_α (calc.).	Δ.
Diethoxythioxan, $C_8H_{16}O_3S$.	In methylal, 49·94	Acetal sulphide, 71·61	
	In CCl_4, 49·85	Less $C_4H_{10}O$ < 22·15	
	In CCl_4 49·79		
	Average = 49·86	49·46	+ 0·40

In calculating the values for acetal sulphide and diethoxythioxan, we have avoided the usual method of adding together the atomic effects, since in complex substances which contain so many atoms in the molecule the slight errors involved in the atomic refractivities are multiplied many times. We have instead used the method which Eykman (*Rec. trav. chim.*, 1893, **12**, 157, 268) emphatically recommends on other grounds; thus the refractive power of a substance closely allied to the compound in question is taken as a basis and then modified in the required manner. It is also necessary to point out that in calculating the value for diethoxythioxan from that of acetal sulphide we have assumed that ring formation has no effect; this is in harmony with the assumption generally made in refractometric work, and it is further justified by the work of Brühl on epichlorohydrin (*Ber.*, 1891, **24**, 657) and paracetaldehyde (*Annalen*, 1880, **203**, 43), in which the formation of oxygen rings was shown to have no effect on refractivity. The formation of cyclic systems has been studied also by Eykman (*Ber.*, 1892, **25**, 3069) in the piperidine series, and by Willstätter (*Ber.*, 1907, **40**, 3982) and Wallach (*Annalen*, 1907, **353**, 331) in the *cyclo*paraffins, and these observers agree that cyclic formation is without effect on the refractive power.

It must be admitted that with the thioxan derivative the difference between the calculated and observed values is small—about 0·4 unit—in comparison with that observed with the other sulphur compounds. But the value which we quote is the mean of three observations, each with different samples of the substance and in different solvents; moreover, the anomaly is of the same order as that observed by Brühl in pyrrole (−0·37), acrolein (+0·34), ethyl crotonate (+0·44), and other carbon compounds. We therefore consider that diethoxythioxan shows a small but quite perceptible exaltation.

The general conclusions to be drawn from the refractivities of these bivalent-sulphur compounds is that a normal or abnormal state of the reactivity of the sulphur is accompanied by a corresponding state of the refractive power of the substance; but at present it is impossible to say whether any quantitative relation holds between the chemical and the physical anomaly.

Leaving the thioxan derivative for a moment out of the question, it is further evident that all the substances dealt with conform to the law laid down by Brühl, since the abnormal compounds contain the bivalent sulphur adjacent to other unsaturated atoms and the normal ones do not. Moreover, the depressed reactivity of the optically anomalous compounds may be explained by the assumption that the residual affinity of the bivalent sulphur which endows this element with additive properties is at least partly saturated by that of the adjacent unsaturated atoms.

In the light of this evidence, taken from various types of bivalent-sulphur compounds, the step to the thioxan derivative is clearly indicated. Thus it seems that the unsaturated sulphur of this compound must be "conjugated" with another unsaturated group, which, from reasons previously mentioned, is probably the cyclic oxygen in the 1:4-position with respect to the sulphur atom.

EXPERIMENTAL.

Acetal Sulphide.—An alcoholic solution containing 50 grams of chloro-acetal with about one and a-half times the calculated quantity of sodium sulphide was heated on the water-bath for twenty-four hours. The alcohol was then removed by distillation, and the residue faintly acidified with dilute sulphuric acid. The free hydrogen sulphide remaining in solution was expelled by blowing a rapid current of air through the mixture at the atmospheric temperature. Finally the oily layer, which consisted of the required sulphide and unchanged chloroacetal, was separated by repeated extraction with ether. The united extracts were dried and distilled, first on the water-bath, and finally under diminished pressure. The yield was about 30 grams of acetal sulphide, a colourless oil boiling at 147—148°/12 mm.:

0·1028 gave 0·2021 CO_2 and 0·0874 H_2O. C=53·6; H=9·44.
$C_{12}H_{26}O_4S$ requires C=54·1; H=9·77 per cent.

The refractive index and density of a pure sample were determined:

$$d_{23\cdot5^\circ} = 0\cdot9863\ ;\quad d_{17\cdot5^\circ} = 0\cdot9918.$$
$$n_{D(23\cdot5^\circ)} = 1\cdot44734\ ;\quad n_{\alpha\,17\cdot5^\circ} = 1\cdot44659.$$

whence, according to the Lorenz-Lorentz formula, the molecular refractive power is:

$$M_D = 71\cdot95 \quad \text{and} \quad M^{\alpha} = 71\cdot61.$$

Additive products with mercuric halides.—An aqueous-alcoholic solution of acetal sulphide, when mixed with mercuric chloride solution, at once yields a precipitate of the double salt. A sample of this substance was recrystallised from alcohol, and was thus obtained in well-defined needles, which melted at 70°:

0·1888 gave 0·1848 CO_2 and 0·0792 H_2O. C = 26·71; H = 4·66.

$C_{12}H_{26}O_4S,HgCl_2$ requires C = 26·81; H = 4·84 per cent.

Acetal sulphide mercurichloride is insoluble in water, and easily soluble in alcohol or acetone.

Mercuric iodide, when shaken with an acetone solution of acetal sulphide at the atmospheric temperature, gives a copious, crystalline precipitate of the double salt. It melts at 68°, and is sparingly soluble in ether or in cold alcohol; when set aside the substance decomposes into the constituents.

Action of Ethyl Iodide on Acetal Sulphide in Presence of Mercuric Iodide.

Equimolecular proportions of acetal sulphide and mercuric iodide were shaken at the atmospheric temperature with an excess of ethyl iodide (10 c.c. for every gram of acetal sulphide). In about half an hour the mercuric iodide had completely dissolved, indicating the commencement of formation of the sulphonium salt. After five hours had elapsed, the excess of alkyl iodide was removed by a rapid current of air, and the oily residue was set aside to crystallise. The semi-solid mass was repeatedly extracted with ether, which removed an unstable mercuric iodide double salt, and the residue of sulphur yellow leaflets, after further purification, was analysed:

0·1624 gave 0·1161 CO_2 and 0·0593 H_2O. C = 19·48; H = 3·92.

$C_{14}H_{31}O_4I_3SHg$ requires C = 19·18; H = 3·54 per cent.

Diacetalethylsulphonium mercuri-iodide melts at 43°, and is soluble in alcohol or acetone and sparingly so in ether. About one and a-half grams of purified material were obtained from one gram of acetal sulphide.

Acetal sulphide and excess of hydrogen dioxide were mixed in acetone solution, and kept for twenty-four hours. The oily product which remained after evaporating the solvent could not be purified, since it decomposed on being heated and could not be solidified. Attempts to convert it to solid derivatives with mercuric halides or by means of dry hydrogen chloride to obtain a thioxan derivative were also unsuccessful. Apparently the conversion of the acetal sulphide is almost complete, since no diethoxythioxan could be isolated by treatment with hydrochloric acid. The substance, which is almost certainly the sulphoxide, is distinguished from the acetal sulphide by much greater solubility in water.

Diethoxythioxan.

Dry hydrogen chloride was rapidly passed for a few minutes through a solution of acetal sulphide in absolute alcohol or dry ether. On evaporating the solvent as quickly as possible under diminished pressure, diethoxythioxan remained as a mass of colourless crystals. The reaction appears to be almost quantitative, since 2·46 grams of acetal sulphide gave 1·75 grams of thioxan derivative, whilst theory requires 1·77 grams.

The substance may be purified by crystallisation from alcohol or by sublimation, which frequently yields crystals more than one inch in length. In either case the product melts at 101°; it is soluble in hot water and in most organic media:

0·1142 gave 0·2062 CO_2 and 0·0902 H_2O. C = 49·2; H = 8·7.
$C_8H_{16}O_3S$ requires C = 50·0; H = 8·3 per cent.

The molecular weight was determined by the cryoscopic method:

0·2691 in 16·48 benzene gave $\Delta^t = -0·423°$. M.W. = 189.
$C_8H_{16}O_3S$ requires M.W. = 192.

The refractivity of the substance in carbon tetrachloride and methylal was determined with purified samples from three different preparations:

I. *In Carbon Tetrachloride.*

Solvent: $d_{18^\circ} = 1·6014$; $n_\alpha = 1·4587$; wt. = 8·5873.
Solution: $d_{18^\circ} = 1·5704$; $n_\alpha = 1·4597$; wt. = 8·9590.
$M_\alpha = 49·85$.

II. *In Carbon Tetrachloride.*

Solvent: $d_{18^\circ} = 1·6014$; $n_\alpha = 1·45757$; wt. = 7·9754.
Solution: $d_{18^\circ} = 1·5484$; $n_\alpha = 1·45921$; wt. = 8·5904.
$M_\alpha = 49·79$.

III. *In Methylal.*

Solvent: $d_{18^\circ}=0{\cdot}86315$; $n_\alpha=1{\cdot}35192$; wt. = 3·8958.
Solution: $d_{18^\circ}=0{\cdot}87439$; $n_\alpha=1{\cdot}35792$; wt. = 4·1424.
$M_\alpha=49{\cdot}94$.

Diethoxythioxan may be crystallised from a boiling 10 per cent. aqueous solution of sodium hydroxide; it does not reduce warm Fehling's solution, cold neutral or acid permanganate solutions, or ammoniacal silver solution. Also the substance is not attacked by concentrated alcoholic or aqueous ammonia at 150°; it is very soluble in concentrated aqueous hydrochloric acid, being decomposed thereby, and on evaporating the solution under diminished pressure, an amorphous substance is deposited. Concentrated sulphuric acid freely dissolves the substance, giving a red solution. Additive products with mercuric chloride or iodide could not be obtained by mixing these substances with an acetone or alcoholic solution of diethoxythioxan; it may be recalled that such additive products are readily obtained from acetal sulphide under similar conditions.

Diethoxythioxan seems unattacked by hydrogen dioxide under the same conditions as those described with acetal sulphide, since almost the entire amount of the original material could be isolated after treatment.

Action of Ethyl Iodide in Presence of Mercuric Iodide.—A solution in ethyl iodide of diethoxythioxan (1 gram for every 10 c.c. of ethyl iodide) and mercuric iodide in equimolecular proportions was set aside at the atmospheric temperature. After eight hours, a portion of the mixture was examined, but no sulphonium salt could be isolated. In fifteen hours, there were signs that reaction had commenced, since a small quantity of the mercuric halide had passed into solution; but the mixture was not more closely examined until a further nine hours had elapsed. The liquid was then filtered from the undissolved mercuric iodide, and the ethyl iodide was removed from the filtrate by a rapid current of air. The yellow oil which remained was unstable, and, if allowed to remain exposed to the atmosphere, readily deposited mercuric iodide; but before profound decomposition had taken place, the mixture was repeatedly extracted with dry ether, and thus a stable and almost colourless solid was obtained in the proportion of half a gram to every gram of diethoxythioxan taken. After purification, it melted at 95—97°:

0·1028 gave 0·0562 CO_2 and 0·0230 H_2O. C = 14·9; H = 2·48.
$C_{10}H_{21}O_3I_3SHg$ requires C = 14·96; H = 2·49 per cent.

The additive compound is readily soluble in acetone, but almost insoluble in water of ether.

It may be mentioned that no signs of reaction between ethyl iodide and the thioxan derivative alone could be detected after the mixture had remained for four days at the atmospheric temperature.

In conclusion, we wish to thank Dr. Stewart for criticism of the theoretical part of this paper. We also wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this investigation.

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CXIV.—*The Influence of Hydroxy- and Alkyloxy-groups on the Velocity of Saponification. Part II.*

By ALEXANDER FINDLAY and EVELYN MARION HICKMANS, M.Sc.

IN Part I of this investigation (Findlay and Turner, Trans., 1905, **87**, 747) attention was drawn to the considerable increase in the value of the saponification constant by the substitution of hydrogen by a phenyl or alkyloxy-group, and to a still greater extent by the hydroxyl group; the esters then investigated being ethyl phenylacetate, methyl, ethyl, and propyl mandelates, and ethyl methoxy-, ethoxy-, and propoxyacetates. In order to obtain a wider knowledge of the influence, more especially of the hydroxyl group, on the velocity of saponification, the previous investigation has been extended so as to include the ethyl esters of α-hydroxy-β-phenylpropionic acid, β-hydroxy-β-phenylpropionic acid, γ-hydroxy-γ-phenylbutyric acid, glycollic acid, and lactic acid. We have also determined the velocities of saponification of ethyl propionate, ethyl phenylpropionate, and methyl phenylacetate.

Since the velocity of saponification of several of these esters is very high, the measurements were carried out by the conductivity method (Walker, *Proc. Roy. Soc.*, 1906, *A*, **78**, 157). With the exception of ethyl β-hydroxy-β-phenylpropionate, ethyl γ-hydroxy-γ-phenylbutyrate and ethyl phenylpropionate, all of which are too sparingly soluble in water, the velocities of saponification were determined both in aqueous solution and in 30 per cent. aqueous alcohol (by weight). The temperature was in all cases 25°. The values of the saponification constants obtained are as follows:

Ester.	$K_{(\text{water})}$.	$K_{(\text{alcohol})}$.
Ethyl glycollate	75	54
,, lactate	63·5	38
,, α-hydroxy-β-phenylpropionate	40·1	27
,, γ-hydroxy-γ-phenylbutyrate	[16·5]	11·0
,, phenylpropionate	[6·9]	3·05
,, propionate	5·3	2·4
,, β-hydroxy-β-phenylpropionate	[4·9]	3·3
Methyl phenylacetate	27·4	11·2

The values of $K_{(\text{water})}$ enclosed in brackets were obtained by calculation from the values in aqueous-alcoholic solution. Before doing so, however, it was necessary to discover whether the ratio $K_{(\text{water})}/K_{(\text{alcohol})}$ is the same in the case of different esters. We calculated this ratio, therefore, not only for the esters given in the table above, but also for those investigated previously by Findlay and Turner (*loc. cit.*). As a result, it was found that the values of the ratio are very fairly concordant, the mean value being 1·5, except in the case of ethyl propionate and methyl phenylacetate. In the case of these two esters, the value of the ratio is 2·3 and 2·4 respectively. In order to obtain the values of the saponification constants of ethyl β-hydroxy-β-phenylpropionate and of ethyl γ-hydroxy-γ-phenylbutyrate, the values of $K_{(\text{alcohol})}$ were multiplied by 1·5, whereas, in the case of ethyl phenylpropionate, the factor employed was 2·3. Justification for this is given by the fact that with the factor 1·5, the value of $K_{(\text{water})}$ for ethyl phenylpropionate would be lower than that for ethyl propionate, whereas, in the case of analogous compounds, the phenyl group raises the saponification constant.

On looking through the above table, the greatly augmenting influence of the hydroxyl group on the velocity of saponification is again observed, as is shown in the case of ethyl glycollate, ethyl lactate, and ethyl α-hydroxy-β-phenylpropionate. With regard to the first two, it may be mentioned that the impression given by the text-books is that these esters are saponified with immeasurably great velocities. It will, however, be seen that this is by no means the case. The velocity of saponification certainly is great, but it is quite measurable, and is, indeed, very much less than that of methyl mandelate, which was investigated previously.

Influence of the Phenyl Group.—The influence of the phenyl group on the velocity of saponification is seen from the following table, where K_1 is the saponification constant of the former of each pair of esters compared, and K_2 that of the latter.

Esters.	K_1/K_2.
Methyl phenylacetate : methyl acetate	2·3
Ethyl phenylacetate : ethyl acetate	1·9
,, phenylpropionate : ethyl propionate	1·3
,, mandelate : ethyl glycollate	0·88
,, α-hydroxyphenylpropionate : ethyl lactate	0·63

The above figures are remarkable. Whereas the introduction of the phenyl group into propionic acid or acetic acid raises the value of the saponification constant of the ethyl and methyl esters, introduction of the phenyl group into glycollic acid or lactic acid, both of which contain the hydroxyl group, markedly lowers the value of the constant. In the case of the first three pairs of esters, not containing the hydroxyl group, the influence of the phenyl group diminishes with increase in the molecular weight of the ester.

Influence of the α-Hydroxyl Group.—As has already been pointed out, the introduction of an hydroxyl group has a greatly accelerating influence on the velocity of saponification. This is made very clear from the following table, where K_1/K_2 gives the ratio of the saponification constants of the different pairs of esters.

Esters.	K_1/K_2.
Ethyl glycollate : ethyl acetate	11·5
,, lactate : ethyl propionate	11·95
Methyl mandelate : methyl phenylacetate	5·7
Ethyl mandelate : ethyl phenylacetate	5·3
,, α-hydroxyphenylpropionate : ethyl phenylpropionate	5·8

Just as the phenyl group has a much smaller (in fact, negative) influence when introduced into an ester containing the hydroxyl group than in the case of a non-hydroxylated ester, so here, we find that the influence of the hydroxyl group, although in all cases exercising an accelerating influence on the velocity of saponification, has a much greater influence in the case of esters not containing the phenyl group than in the case of those in which the phenyl group is present. We find here, therefore, a very marked antagonistic action between the phenyl and hydroxyl groups when introduced into the same molecule. Such an effect is not observed in the case of the affinity constants of the acids.

Reference may be made here to the effect of substitution in the case of the methyl esters as compared with that in the case of the ethyl esters. It was pointed out in the previous communication (p. 751) that the value of the saponification constant of methyl mandelate calculated from the saponification constant of methyl acetate and the influence of the phenyl and hydroxyl groups, as determined in the case of the ethyl ester, gave too low a value. The reason for this we see partly in the increased value of the influence of the phenyl and hydroxyl groups, but to a greater degree it is due to the fact that the value for the saponification constant of methyl acetate, which we had calculated from the determinations of Reicher, was too low, namely, 9·66 instead of 11·7, the value more recently determined by Walker (*loc. cit.*). On the basis of the factors previously employed, the calculated value for the saponification constant of methyl mandelate would be 11·7 × 1·8 ×

5·3 = 112, instead of 92, previously calculated; the experimentally determined value being 157.

Influence of the β- and γ-Hydroxyl Group.—With regard to the influence of the hydroxyl group in the β- or γ-position, the rather unexpected result was obtained that the saponification constant of ethyl β-hydroxy-β-phenylpropionate is much less than that of ethyl γ-hydroxy-γ-phenylbutyrate.

Relation between Saponification Constant and Strength of Acid.—It has from time to time been discussed whether the velocity of saponification of an ester by an alkali is connected with the strength of the acid from which the ester is derived. Conrad and Brückner (*Zeitsch. physikal. Chem.*, 1891, **7**, 290) concluded, on the basis of their own determinations and those previously carried out by Reicher, that the velocity of saponification . . . . of the esters of the mono- and poly-basic acids of the fatty series increases with the strength of the acid. Doubt has been expressed as to the universality of this conclusion, for example, by Hjelt, but it would appear from the investigations of Hjelt himself (*Ber.*, 1898, **31**, 1844) on the saponification velocity of the ethyl ester of acids of the succinic acid series, as well as from experiments by Sudborough and Feilmann (Proc., 1897, **13**, 241), that in the case of homologous acids, or in the case of the introduction of similar groups, the velocities of saponification do follow the order of the affinity constants of the acids.

Qualified support is given to this view by our own experiments. In the table following we have arranged the values of the saponification constants (K_e) of the ethyl esters in aqueous solution in order of decreasing values, incorporating also the esters investigated previously by Findlay and Turner. In the third column of the table are given the values of the affinity constants (100 k) of the acids, as determined by Ostwald (*Zeitsch. physikal. Chem.*, 1889, **3**, 170, 241) and by Findlay, Turner, and Owen (this vol., 938).

	K_e.	100 k.
Ethyl glycollate	75	0·0150 (O.)
,, mandelate	66	0·0417 (O.)
,, lactate	63·5	0·0138 (O.)
,, α-hydroxyphenylpropionate	40·1	0·019 (F., T. & O.)
,, phenylmethoxyacetate	23·3	0·074 (F., T. & O.)
,, γ-hydroxy-γ-phenylbutyrate	16·5	—
,, phenylethoxyacetate	15·7	0·053 (F., T. & O.)
,, phenylpropoxyacetate	13·3	0·049 (F., T. & O.)
,, phenylacetate	12·4	0·0056 (O.)
,, phenylpropionate	6·9	0·0023 (O.)
,, acetate	6·5	0·0018 (O.)
,, propionate	5·3	0·0013 (O.)
,, β-hydroxy-β-phenylpropionate	4·9	0·0040 (F., T. & O.)

From the above table it will at once be seen that the connexion between saponification constant of the ethyl ester and the affinity constant of the corresponding acid is by no means one of direct proportion or of symbatic variation. Thus, ethyl glycollate ($K_e = 75$) has a much higher saponification constant than ethyl methoxyacetate ($K_e = 23·3$), but the affinity constant of glycollic acid ($100\ k = 0·015$) is considerably less than that of phenylmethoxyacetic acid ($100\ k = 0·074$). Even phenylpropoxyacetic acid is a considerably stronger acid ($100\ k = 0·049$) than glycollic acid, although the saponification constants of their ethyl esters are as 13 to 75. A like behaviour is found in the case of glycollic and mandelic acids and of their ethyl esters. Moreover, ethyl mandelate and ethyl lactate have saponification constants of not greatly differing value, although the affinity constant of mandelic acid ($100\ k = 0·0417$) is three times greater than the affinity constant of lactic acid ($100\ k = 0·0138$). One could not, of course, expect anything like exact proportionality between the affinity constant of the acid and the saponification constant of the ester derived from it; but neither can we maintain in view of the examples given and of others which are contained in the above table, that the saponification constants of esters are directly dependent on, or even vary in the same direction as, the affinity constants of the acids from which they are derived. It appears certainly to be true that in the case of homologous series, the affinity constant of the acids and the saponification constants of the esters decrease with increasing molecular weight (for example, phenylmethoxy-, phenylethoxy-, and phenylpropoxy-acetic acids), but it appears to be very doubtful whether any general connexion exists between the two factors.

Certainly the cases we have investigated do not point in that direction.

EXPERIMENTAL.

Ethyl α-Hydroxy-β-phenylpropionate.—The free acid was prepared by Conrad's method (*Annalen*, 1881, **209**, 242). From this the ester was obtained by heating with absolute alcohol on a water-bath for nine to ten hours in presence of anhydrous hydrogen chloride. The ester thus obtained boiled at 156°/20 mm.

Velocity of Saponification in Aqueous Solution.

$N/250$ ester; $N/251$ NaOH.

(*a*) $K = 40·2$ (extreme values 42·7 and 38·2).
(*b*) $K = 39·9$ (,, ,, 41·7 ,, 38·0).

General mean: $K = 40·1$.

Saponification in 30 per cent. Alcohol.

N/250 ester ; *N*/251 NaOH.

(*a*) $K=26{\cdot}9$ (extreme values 28·4 and 25·5).
(*b*) $K=27{\cdot}2$ (,, ,, 28·9 ,, 25·8).
General mean : $K=27{\cdot}0$.

Ethyl β-Hydroxy-β-phenylpropionate.—The acid was prepared from cinnamic acid by Fittig and Binder's method (*Annalen*, 1879, **195**, 136), and was converted into its ethyl ester as in the preparation of the previous ester. The ester boiled at 135°/9—10 mm. The ester was too sparingly soluble in water to allow of determining its saponification velocity in aqueous solution.

Saponification in 30 per cent. Alcohol.

N/240 ester ; *N*/240·6 NaOH.

(*a*) $K=3{\cdot}38$ (extreme values 3·44 and 3·30).
(*b*) $K=3{\cdot}20$ (,, ,, 3·27 ,, 3·13).
General mean : $K=3{\cdot}3$.

Ethyl γ-Hydroxy-γ-phenylbutyrate.—The lactone was prepared by the reduction of benzoylpropionic acid with sodium amalgam. The crystals melted at 35—36° :

0·1714 gave 0·4627 CO_2 and 0·0988 H_2O. C = 73·62 ; H = 6·40.
$C_{10}H_{10}O_2$ requires C = 74·0 ; H = 6·17 per cent.

The ethyl ester was obtained by heating the lactone on the water-bath for nine hours with three times its weight of absolute alcohol in presence of dry hydrogen chloride. It was obtained as a colourless liquid boiling at 152—153°/12 mm.

Saponification in 30 per cent. Alcohol.

N/240 ester ; *N*/240·6 NaOH.

(*a*) $K=10{\cdot}8$ (extreme values 11·5 and 10·1).
(*b*) $K=11{\cdot}2$ (,, ,, 12·5 ,, 10·4).
General mean : $K=11{\cdot}0$.

Ethyl Glycollate.—This was obtained from Kahlbaum, and was redistilled.

Saponification in Aqueous Solution.

N/100 ester ; *N*/100 NaOH.

(*a*) $K=73{\cdot}6$ (extreme values 77·3 and 70·5).
(*b*) $K=75{\cdot}8$ (,, ,, 77·3 ,, 72·6).
General mean : $K=75$.

Saponification in 30 per cent. Alcohol.

The values of K showed a general tendency to increase during saponification. As approximate value we may take $K=54$.

Ethyl Lactate.—Obtained from Kahlbaum.

Saponification in Aqueous Solution.

$N/100$ ester ; $N/100$ NaOH.

(*a*) $K=63{\cdot}7$ (extreme values 64·4 and 63·0).
(*b*) $K=63{\cdot}2$ (,, ,, 65·4 ,, 62·0).
General mean : $K=63{\cdot}5$.

Saponification in 30 per cent. Alcohol.

$N/198$ ester ; $N/198$ NaOH.

(*a*) $K=39{\cdot}2$ (extreme values 41·6 and 37·8).
(*b*) $K=37{\cdot}2$ (,, ,, 41·0 ,, 35·7).
General mean : $K=38$.

Ethyl Propionate.—Obtained from Kahlbaum.

Saponification in Aqueous Solution.

$N/250$ ester ; $N/251$ NaOH.

(*a*) $K=5{\cdot}21$ (extreme values 6·30 and 4·27).
(*b*) $K=5{\cdot}31$ (,, ,, 6·12 ,, 4·07).
General mean : $K=5{\cdot}3$.

Saponification in 30 per cent. Alcohol.

$N/250$ ester ; $N/251$ NaOH.

(*a*) $K=2{\cdot}31$ (extreme values 2·62 and 2·10).
(*b*) $K=2{\cdot}39$ (,, ,, 2·52 ,, 2·29).
General mean : $K=2{\cdot}4$.

Ethyl Phenylpropionate.—Obtained from Kahlbaum.

Saponification in 30 per cent. Alcohol.

$N/240$ ester ; $N/240{\cdot}6$ NaOH.

(*a*) $K=3{\cdot}01$ (extreme values 3·17 and 2·86).
(*b*) $K=3{\cdot}10$ (,, ,, 3·42 ,, 2·62).
General mean : $K=3{\cdot}05$.

Methyl Phenylacetate.—Obtained from Kahlbaum.

Saponification in Aqueous Solution.

$N/251$ ester ; $N/251$ NaOH.

(*a*) $K=27{\cdot}1$ (extreme values $32{\cdot}5$ and $24{\cdot}8$).
(*b*) $K=27{\cdot}6$ (,, ,, $32{\cdot}5$,, $24{\cdot}8$).
General mean : $K=27{\cdot}4$.

Saponification in 30 *per cent. Alcohol.*

$N/240$ ester ; $N/240{\cdot}6$ NaOH.

a) $K=11{\cdot}31$ (extreme values $11{\cdot}74$ and $11{\cdot}05$).
b) $K=11{\cdot}07$ (,, ,, $11{\cdot}62$,, $10{\cdot}73$).
General mean : $K=11{\cdot}2$.

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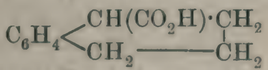
CXV.—*Optically Active Reduced Naphthoic Acids. Part IV. Comparison of the Rotatory Powers of the Di- and Tetra-hydronaphthoic Acids with those of Phenylallylacetic, α-Phenylvaleric, β-Phenyl-α-ethyl-, and β-Phenyl-α-methyl-propionic Acids.**

By ROBERT HOWSON PICKARD and JOSEPH YATES.

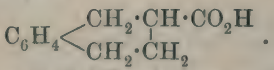
VON BAEYER (*Annalen*, 1891, **266**, 169 *et seq.*) has described six reduced naphthoic acids, in which the carboxyl group is attached to the reduced ring, and four of which contain an asymmetric carbon atom. Three of these, the two tetrahydro-acids and Δ^2-dihydro-1-naphthoic acid, have already been resolved into their optically active components (Trans., 1905, **87**, 1763 ; 1906, **89**, 1101, 1484), and the work has now been completed by the preparation of the active forms of Δ^3-dihydro-2-naphthoic acid.

The structure of these bicyclic acids can be compared with that of certain monocyclic acids ; thus, for example :



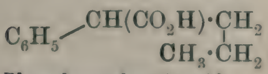
$C_6H_4<\begin{matrix}CH(CO_2H)\cdot CH_2\\ CH_2 \text{———} CH_2\end{matrix}$

1 : 2 : 3 : 4-Tetrahydro-1-naphthoic acid.



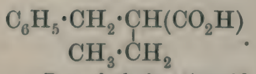
$C_6H_4<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot CH_2\end{matrix}$.

1 : 2 : 3 : 4-Tetrahydro-2-naphthoic acid.



$C_6H_5\diagup\begin{matrix}CH(CO_2H)\cdot CH_2\\ CH_3\cdot CH_2\end{matrix}$

Phenylpropylacetic acid.
(α-Phenylvaleric acid.)



$\begin{matrix}C_6H_5\cdot CH_2\cdot CH(CO_2H)\\ CH_3\cdot CH_2\end{matrix}$.

Benzylethylacetic acid.
(β-Phenyl-α-ethylpropionic acid.)

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* For the purpose of comparison these last three acids are referred to as phenylpropyl-, benzylethyl-, and benzylmethyl-acetic acids respectively in this paper.

The main difference between these two types of acid lies in the mono- or bi-cyclic structure. As the former, like the reduced naphthoic acids, possess an asymmetric carbon atom in their molecule, it was thought desirable to extend the investigation to include the resolution of these, in the hope that the results would throw some light on the question of the relation between optical activity and chemical constitution.

All the acids, which have now been resolved, form stable salts with *l*-menthylamine, and the mixture of the *l*B*d*A and *l*B*l*A salts is readily separated by fractional crystallisation. It is believed that the active acids are pure, and have been completely resolved, as in each case after obtaining from one solvent the pure menthylamine salt of constant rotation, it was found that the rotation remained unaltered by crystallisation of the salt from another solvent. Evidence in favour of this is shown in those cases where the two isomerides have been obtained of equal and opposite rotatory powers, whilst in the case of benzylmethylacetic acid we obtained a product with a rotation the same as that given by Kipping and Hunter (Trans., 1903, **83**, 1008), who resolved this acid by means of the quinine salt.

The molecular rotations of the acids and their sodium salts are shown in the following table.

Molecular Rotations.

	Acid in $CHCl_3$.	Acid in C_6H_6.	Sodium salt in H_2O.
Δ^2-Dihydro-1-naphthoic acid ……………	370·4°	309·5°	374·5°
Δ^3-Dihydro-2-naphthoic ,, ……………	276·2	317·0	308·9
1 : 2 : 3 : 4-Tetrahydro-1-naphthoic acid..	28·1	92·1	21·1
1 : 2 : 3 : 4-Tetrahydro-2-naphthoic ,, ..	91·2	87·9	90·5
Phenylallylacetic acid ……………………	148·9	181·6	40·2
Phenylpropylacetic acid …………………	104·7	140·7	5·0
Benzylethylacetic acid…… ……………	68·3	73·0	100·7
Benzylmethylacetic acid…………………	45·5	44·4	66·8

It is obvious that these results indicate that very little definite evidence on the relationship between chemical constitution and rotatory power can as yet be obtained by a comparison of the rotatory powers of such acids when dissolved in various solvents. Phenomena, such as the association of the free acids with the solvents or the varying degrees of ionisation of the aqueous solutions of the sodium salts,* undoubtedly have a large influence on the rotations, and prevent any very definite conclusions on the above question.

The general deductions, however, to be drawn from these results may be summarised as follows :

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* Compare the results obtained by Kipping (this vol., p. 416) for the specific rotation in water of mandelic acid and its salts.

(*a*) The influence of unsaturation is evidenced by the relatively high rotations of the dihydro-1- and -2-naphthoic acids and phenylallylacetic acid as compared with the rotations of the corresponding tetrahydro-acids and phenylpropylacetic acid.

(*b*) The relative position of the asymmetric atom to the aromatic ring appears to have less effect on the rotation than the influence of the double bond, for the tetrahydro-1-acid has a lower rotation than the tetrahydro-2-acid, whereas the dihydro-1-acid has a higher rotation than the dihydro-2-acid.

(*c*) The bicyclic compounds have, as a rule, the larger rotations, as is shown in the case of dihydro-1-naphthoic acid compared with phenylallylacetic acid and that of tetrahydro-1-naphthoic acid compared with phenylpropylacetic acid; there is, however, a possible exception to this in the cases of tetrahydro-2-naphthoic acid and benzylethylacetic acid.

The influence on the rotation of a change from an open-chain to a cyclic compound has been previously observed in the case of several acids and their anhydrides or lactones. In general, it may be said that the rotation is higher in the case of the ring compound, although there are exceptions, as, for example, in the case of camphoric acid and its anhydride (Aschan, *Ber.*, 1894, **27**, 2011).

(*d*) It has been observed that the relative proximity of a double linking frequently tends to increase the rotations of closely related unsaturated compounds (compare Rupe, *Annalen*, 1903, **327**, 157), so that the higher rotations of the two dihydro-acids (in which the distance of the asymmetric carbon atom from the double bond is the some in both) may be due, not only to their cyclic character, but also, in part, to the closer proximity of the double linking to the asymmetric carbon atom in these than in the phenylallylacetic acid.

This is further borne out by the much greater difference between the rotations of the dihydro-acids and phenylallylacetic acid than between the rotations of the tetrahydro-acids and phenylpropylacetic and benzylethylacetic acids.

EXPERIMENTAL.

Preparation of Δ^3-Dihydro-2-naphthoic Acid.

The method described by Baeyer, Schoder, and Besemfelder (*Annalen*, 1880, **206**, 169) for the preparation of Δ^3-dihydro-2-naphthoic acid was adopted with the slight modifications described below.

2-Naphthoic acid was dissolved in potassium carbonate and reduced at 0° by means of sodium amalgam, a stream of carbon dioxide being passed through the liquid to neutralise the sodium hydroxide formed. The reduction was continued until a test portion oxidised with potassium permanganate did not give a precipitate when acidified with sulphuric acid. After removal of the mercury, the liquid was acidified, and yielded an impure acid melting at about 88°. This was dissolved in a solution of potassium hydrogen carbonate, and sufficient hydrochloric acid added to precipitate about one-quarter of the dissolved acid. This precipitate melted at 152°, and consisted chiefly of the stable acid. The mother liquor was next fully acidified, and the acid obtained was crystallised from water. The labile acid was thus isolated in small needles melting at 103°.

Resolution of Δ^3-*Dihydro-2-naphthoic Acid.*

1-*Menthylamine* d-Δ^3-*Dihydro-2-naphthoate.*—The racemic acid (1 mol.) was dissolved in the calculated quantity of a solution of potassium hydrogen carbonate and mixed with a solution of *l*-menthylamine hydrochloride (1 mol.). The *l*B*d*A and *l*B*l*A salts were precipitated as a white solid, which melted indefinitely at 140—150° and had $[\alpha]_D$ $-16{\cdot}6°$ in ethyl alcohol. It was soluble in most organic media, and sparingly so in light petroleum. By repeated crystallisation, first from dilute alcohol, then from absolute alcohol, and lastly from acetone, the pure *l*B*d*A salt, melting at 143—144° and possessing a constant specific rotation, was obtained:

0·3138, made up to 20 c.c. with ethyl alcohol, gave* α $+2{\cdot}40°$; whence $[\alpha]_D$ $+76{\cdot}48°$ and $[M]_D$ $+251{\cdot}62°$.

0·4292 was boiled with excess of sodium hydroxide until all the menthylamine was expelled, when it was found that 0·0556 NaOH had been neutralised.† The calculated amount is 0·0522 NaOH.

d-Δ^3-*Dihydro-2-naphthoic Acid.*—The pure *l*B*d*A salt was decomposed by dilute hydrochloric acid, and the acid extracted with ether. After crystallisation from water, it melted at 101°:

0·4242 neutralised 0·0984 NaOH. This amount of an acid, $C_{11}H_{10}O_2$, requires 0·0975 NaOH.

0·3604, made up to 20 c.c. with chloroform, gave α $+5{\cdot}72°$; whence $[\alpha]_D$ $+158{\cdot}71°$ and $[M]_D$ $+276{\cdot}15°$.

0·3194, made up to 20 c.c. with benzene, gave α $+5{\cdot}82°$; whence $[\alpha]_D$ $+182{\cdot}21°$ and $[M]_D$ $+317{\cdot}04°$.

The *sodium* salt separates out in white, flaky crystals when the calculated amount of sodium ethoxide is added to a solution of the acid in anhydrous alcohol. It was washed with a mixture of alcohol and ether, and dried in a desiccator:

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* All rotations recorded in this paper were observed in a 2-dcm. tube unless otherwise stated.

† All the pure menthylamine salts described in this paper have been analysed in a similar manner. In each case, the results showed that the salts were composed of one equivalent each of acid and base.

0·1595 gave 0·0575 Na_2SO_4. Na = 11·68.

$C_{11}H_9O_2Na$ requires Na = 11·73 per cent.

0·3248, made up to 20 c.c. with water, gave α +5·12°; whence $[\alpha]_D$ +157·63° and $[M]_D$ +308·95°.

This solution, after standing three days, had $[\alpha]_D$ +148·4°. A few drops of sodium hydroxide solution were then added and the mixture kept for two days, when the solution was found to be inactive. It was then acidified, and the precipitated acid crystallised from dilute alcohol. It was thus obtained in glistening plates, which melted at 153°.

Baeyer (*loc. cit.*) gives the melting point of the inactive Δ^2-dihydro-2-naphthoic acid as 161°.

Preparation of Phenylallylacetic Acid, $C_6H_5\cdot CH(C_3H_5)\cdot CO_2H$.

The method adopted for the preparation of phenylallylacetic acid was that described by Wislicenus (*Annalen*, 1897, **296**, 361), but was somewhat modified as described below.

Phenylacetic acid was first prepared by hydrolysis of phenylacetonitrile, obtained from benzyl chloride by the action of potassium cyanide. The acid was esterified by boiling with absolute alcohol and a small amount of concentrated sulphuric acid, and the pure ester redistilled once over phosphoric oxide. The ethyl phenylacetate was then condensed with pure ethyl oxalate by means of dry sodium ethoxide, and, after decomposing the sodium derivative with dilute sulphuric acid, diethyl phenyloxalacetate was obtained by extraction with ether. When distilled in a vacuum, it loses carbon monoxide, yielding diethyl phenylmalonate, boiling at 150—153°/9—10 mm.

The allyl derivative, diethyl phenylallylmalonate, was prepared by adding diethyl phenylmalonate (1 mol.) to sodium (1 atom) dissolved in ten times its weight of absolute alcohol, and then a slight excess of freshly distilled allyl iodide. The whole was warmed on a water-bath until neutral to litmus, when the alcohol was distilled off, water added, and the residue extracted with ether. The phenylallylmalonic ester was distilled in a vacuum, and the fraction boiling at 160—170°/12—13 mm. hydrolysed by boiling with an alcoholic solution of sodium ethoxide. After removal of the alcohol by distillation, the mixture was acidified, and the phenylallylacetic acid extracted with ether. It was purified by distillation, when the fraction boiling at 172—178°/16 mm. solidified on cooling to a crystalline cake, which melted at 31°.

Resolution of Phenylallylacetic Acid.

l-*Menthylamine* d-*Phenylallylacetate.*—The racemic acid (1 mol.) was dissolved in the requisite amount of a solution of sodium hydrogen carbonate and mixed with a warm solution of *l*-menthylamine hydrochloride (1 mol.). A pasty solid was at once formed, but this rapidly hardened, and, after standing a short time, was collected and dried. It dissolved readily in all organic media, and, after six successive crystallisations from dilute methyl alcohol, the pure *l*B*d*A salt with a constant specific rotation was obtained. It crystallised in acicular needles, which melted at 145°:

0·3138, made up to 20 c.c. with ethyl alcohol, gave α $-0{\cdot}04°$; whence $[\alpha]_D$ $-0{\cdot}82°$ and $[M]_D$ $-2{\cdot}71°$.

d-*Phenylallylacetic Acid.*—The pure *l*B*d*A salt was decomposed by dilute hydrochloric acid and extracted with ether. After removal of the ether, the acid was obtained as a viscid oil, which did not solidify on long standing in a vacuum desiccator, when subjected to a low temperature, or when seeded with the inactive acid:

0·4835, made up to 20 c.c. with chloroform, gave α $+4{\cdot}09°$; whence $[\alpha]_D$ $+84{\cdot}59°$ and $[M]_D$ $+148{\cdot}88°$.

0·4884, made up to 20 c.c. with benzene, gave α $+5{\cdot}04°$; whence $[\alpha]_D$ $+103{\cdot}19°$ and $[M]_D$ $+181{\cdot}61°$.

The *sodium* salt crystallises from ethyl alcohol in pearly laminæ. After drying at 110°, it gave the following results:

0·1211 gave 0·0438 Na_2SO_4. Na = 11·73.

$C_{11}H_{11}O_2Na$ requires Na = 11·61 per cent.

0·3353, made up to 20 c.c. with water, gave α $+0{\cdot}68°$; whence $[\alpha]_D$ $+20{\cdot}28°$ and $[M]_D$ $+40{\cdot}15°$.

The *magnesium*, *calcium*, *barium*, *zinc*, *cadmium*, and *manganese* salts are soluble in water, whilst the *cupric*, *ferric*, *silver*, *mercuric*, and *mercurous* salts are insoluble. The *lead* salt crystallises well from water.

Attempts to obtain the pure lævo-acid by fractional crystallisation of its cinchonidine salt were not very successful.

The least soluble cinchonidine salt obtained melted at 100°, and had $[\alpha]_D$ $-58{\cdot}9°$ in ethyl alcohol. This salt was not quite pure, since the *l*-phenylallylacetic acid obtained from it had only $[\alpha]$ $-74{\cdot}8°$ in benzene.

Preparation of Phenylpropylacetic Acid (*a-Phenylvaleric Acid*), $C_3H_7{\cdot}CH(C_6H_5){\cdot}CO_2H$.

a-Phenylvaleronitrile, $C_3H_7{\cdot}CH(C_6H_5){\cdot}CN$.—This substance was prepared by a method similar to that given by Rossolymo (*Ber.*, 1889, **22**, 1235). Phenylacetonitrile and propyl iodide are heated together with a large amount of finely-powdered sodium hydroxide, and the product, after addition of water, is extracted with ether. After two distillations, the fraction boiling at 255—261° is collected and hydrolysed.

The method of hydrolysis recommended is to heat the nitrile with hydrochloric acid at 180—190°, but it was found more convenient to boil the nitrile with moderately strong sulphuric acid (3 : 2) for eight to nine hours. The mixture is then diluted with water, extracted with ether, and the acid removed by washing the ether with a solution of sodium hydroxide. From the latter, it is obtained by acidifying and again extracting with ether. The crude acid boiled at 161—163°/10 mm., and, when cooled, solidified to a crystalline mass, which melted at 52°.

Resolution of Phenylpropylacetic Acid.

l-*Menthylamine Phenylpropylacetate.*—The inactive acid was dissolved in a solution of sodium hydrogen carbonate, and an aqueous solution of *l*-menthylamine hydrochloride added in slight excess. The mixture of salts was precipitated at once in a fairly hard state, and, after standing one hour, was filtered and dried on porous tiles. It was soluble in most organic media, and crystallised from acetone or from dilute alcohol in masses of felted needles. After two crystallisations from aqueous alcohol and five from absolute alcohol, the salt melted at 141° and had a constant rotation:

1·0372, made up to 20 c.c. with ethyl alcohol, gave α $-1{\cdot}82°$; whence $[\alpha]_D$ $-17{\cdot}54°$ and $[M]_D$ $-58{\cdot}41°$.

d-*Phenylpropylacetic Acid.*—The pure *l*B*d*A salt was decomposed by dilute hydrochloric acid and extracted with ether. After removal of the ether, the oil was obtained as a viscid oil, which boiled at 165°/14 mm. and had $D_4^{20°}$ 1·047. At the temperature of a mixture of ice and salt, it solidified when seeded with a little of the inactive acid, but melted when removed from the freezing mixture.

The acid in a 50 mm. tube had α $+37{\cdot}75$; whence $[\alpha]_D$ $+72{\cdot}10°$ and $[M]_D$ $+128{\cdot}34°$.

0·8094, made up to 20 c.c. with chloroform, gave α $+4{\cdot}76°$; whence $[\alpha]_D$ $+58{\cdot}81°$ and $[M]_D$ $+104{\cdot}68°$.

0·5870, made up to 20 c.c. with benzene, gave α $+4{\cdot}64°$; whence $[\alpha]_D$ $+79{\cdot}05°$ and $[M]_D$ $+140{\cdot}71°$.

0·3198, exactly neutralised by an aqueous solution of sodium hydroxide and made up to 20 c.c., gave α $+0{\cdot}09°$; whence $[\alpha]_D$ $+2{\cdot}50°$ and $[M]_D$ $+5{\cdot}00°$. The acid obtained from this solution gave in chloroform solution $[\alpha]_D$ $+58{\cdot}0°$.

The *mercurous, copper, ferric*, and *silver* salts are insoluble in water, whilst the *magnesium, calcium, barium, mercuric*, and *manganese* salts are soluble. The *lead* salt dissolves in hot water, and crystallises out on cooling.

Attempts were made to prepare the lævo-isomeride of the acid by fractional crystallisation of the cinchonidine salt of the acid obtained from the more soluble menthylamine salts, but these were not very successful.

The purest cinchonidine salt obtained melted at 128°, and had $[\alpha]_D - 79{\cdot}27^\circ$ in alcohol after seven crystallisations from acetone.

The *l*-acid obtained from this had $[\alpha]_D - 54{\cdot}5^\circ$ in chloroform and $[\alpha]_D - 71{\cdot}83^\circ$ in benzene, whilst the sodium salt had $[\alpha]_D - 1{\cdot}96^\circ$ in water.

Resolution of Benzylethylacetic Acid (*β-Phenyl-a-ethylpropionic Acid*), $C_6H_5{\cdot}CH_2{\cdot}CH(C_2H_5){\cdot}CO_2H$.

The inactive acid was prepared by the reduction with sodium amalgam of phenylangelic acid (Baeyer and Jackson, *Ber.*, 1880, **13**, 118). It was obtained as a colourless oil, boiling at 193°/80 mm.

l-*Menthylamine* d-*Benzylethylacetate.*—The inactive acid (1 mol.) was exactly neutralised by a solution of sodium hydrogen carbonate and mixed with the calculated amount (1 mol.) of an aqueous solution of *l*-menthylamine hydrochloride. The mixture of the two salts of the lævo-base was precipitated as an oil, which, however, soon solidified. It was soluble in most organic solvents, but crystallised readily from aqueous alcohol. After six recrystallisations from this medium, and then from methyl alcohol, the pure *l*B*d*A salt was obtained in stout prisms, which melted at 137°. The specific rotation of the last two crops was constant, and remained unaltered after recrystallisation from acetone:

0·5366, made up to 20 c.c. with ethyl alcohol, gave $\alpha - 0{\cdot}36^\circ$; whence $[\alpha]_D - 6{\cdot}70^\circ$ and $[M]_D - 22{\cdot}31^\circ$.

d-*Benzylethylacetic Acid.*—The menthylamine salt was decomposed by hydrochloric acid and extracted with ether. The viscous oil thus obtained gave the following polarimetric results:

0·4927, made up to 20 c.c. with benzene, gave $\alpha + 2{\cdot}02^\circ$; whence $[\alpha]_D + 40{\cdot}99^\circ$ and $[M]_D + 72{\cdot}96^\circ$.

0·4979, made up to 20 c.c. with chloroform, gave $\alpha + 1{\cdot}91^\circ$; whence $[\alpha]_D + 38{\cdot}36^\circ$ and $[M]_D + 68{\cdot}28^\circ$.

The *sodium* salt crystallises in pearly leaflets from methyl alcohol, in which it is very soluble:

0·3695 gave 0·1307 Na_2SO_4. Na = 11·46.

$C_{11}H_{13}O_2Na$ requires Na = 11·50 per cent.

0·3811, made up to 20 c.c. with water, gave α + 1·92°; whence $[\alpha]_D$ 50·38° and $[M]_D$ + 100·76°.

The *magnesium*, *calcium*, *barium*, *zinc*, and *mercuric* salts are soluble, whilst the *mercurous*, *lead*, *silver*, *copper*, and *ferric* salts are insoluble in water.

Resolution of Benzylmethylacetic Acid (β-Phenyl-α-methylpropionic Acid), $C_6H_5·CH_2·CH(CH_3)·CO_2H$.

Benzylmethylacetic acid has already been resolved by Kipping and Hunter (*loc. cit.*, compare also Kipping and Salway, Trans., 1904, **85**, 448) by the fractional crystallisation of the quinine salt. By means of *l*-menthylamine we obtained the dextro-acid with a rotation the same as that of these investigators.

l-*Menthylamine* d-*Benzylmethylacetate* is obtained free from the *l*B*l*A isomeride after six recrystallisations from acetone, from which it separates in long, silky needles melting at 143°:

1·0467, made up to 20 c.c. with ethyl alcohol, gave α + 1·79°; whence $[\alpha]_D$ + 17·10° and $[M]_D$ + 54·55°.

d-Benzylmethylacetic acid was obtained as a viscid, colourless oil, which boiled at 160°/13 mm. and had $D_4^{20°}$ 1·065.

In a 50 mm. tube it gave α + 12·06°; whence $[\alpha]_D$ + 22·65° and $[M]_D$ + 37·14°.

0·7465, made up to 20 c.c. with benzene, gave α + 2·02°; whence $[\alpha]_D$ + 27·06° and $[M]_D$ + 44·4°.

0·6565, made up to 20 c.c. with chloroform, gave α + 1·82°; whence $[\alpha]_D$ + 27·72° and $[M]_D$ + 45·5°.

Kipping and Hunter give $[\alpha]_D$ + 22·6° as the specific rotation of the acid, and $[\alpha]_D$ + 26° for that of the sodium salt in water. We obtained a rather higher value for the rotation of the salt.

The sodium salt crystallises in beautiful, lustrous plates from a mixture of methyl alcohol and ether. (Found, Na = 12·46 per cent., calculated 12·37 per cent.)

0·4453, made up to 20 c.c. with water, gave α + 1·60°; whence $[\alpha]_D$ + 35·93° and $[M]_D$ + 66·8°.

d-*Benzylmethylacetyl Chloride.*—As the method given by Kipping and Salway for the preparation of the chloride by means of phosphorus pentachloride is very tedious, we attempted to obtain it by means of thionyl chloride. We found that a mixture of the *d*-acid and thionyl chloride when fractionally distilled soon after mixing gave the pure *d*-chloride. Our preparation was a colourless liquid, which boiled at 111°/11 mm. and had $D_4^{20^\circ}$ 1·102. In a 50 mm. tube it gave α +14·48°; whence $[\alpha]_D$ +26·28° and $[M]_D$ +48·0°.

When hydrolysed by warming with a solution of sodium carbonate, it yielded the pure *d*-acid.

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CXVI.—*Relation between Chemical Constitution and Physiological Action in the Tropeines. Part II.*

By HOOPER ALBERT DICKINSON JOWETT and FRANK LEE PYMAN.

IN continuation of our previous work (Trans., 1906, **89**, 357; 1907, **91**, 92) on the relation between chemical constitution and physiological action in the tropeines, we have prepared and submitted to comparative physiological examination a large number of these compounds to determine how far Ladenburg's generalisation may with accuracy be applied. Before giving the results of our experiments, it is necessary to correct a statement with regard to this generalisation. We observed, in the course of our work, that mydriasis is caused by *m*-hydroxybenzoyltropeine, which, according to the generalisation, should be non-mydriatic, and on further examining the previous work in the subject, we found that Ladenburg (*Annalen*, 1883, **217**, 82) himself had stated this to be the case. It seemed strange that this chemist should have enunciated such a generalisation when his own results were in direct contradiction to it; we, therefore, very carefully searched the literature for the original paper, but without success. We then communicated with Prof. Ladenburg, who informed us that he is unable to recollect putting forward this generalisation.

It has, however, been somewhat widely accepted and occurs in the literature and most text-books on the subject, and has served a useful purpose in grouping together the action of various tropeines. Our further investigation has proved that it cannot be strictly applied.

Briefly stated, the generalisation is that for a tropeine to have mydriatic properties it must contain:

(1) a benzene residue,
(2) an aliphatic hydroxyl in the side-chain containing the carboxyl group.

As α-hydroxy-β-2-pyridylpropionyltropeine is a mydriatic, (1) does not hold, and as both *o*- and *m*-hydroxybenzoyltropeines are mydriatic, (2) is not correct.

The detailed physiological results of this investigation will be communicated elsewhere, but the preparation and chemical properties of several new tropeines are described in this paper. Several tropeines which have previously been described in chemical literature were prepared for the purpose of physiological examination, and these have been further characterised by the preparation of a number of new salts. We will here briefly refer to some of the more important physiological results.

Atroglyceryltropeine, which contains two hydroxy-groups in the acyl residue corresponding with those of both atropine and homatropine, is intermediate between these in mydriatic value.

a-Hydroxy-β-phenylpropionyltropeine has greater mydriatic properties than homatropine, and *a-hydroxy-β-2-pyridylpropionyltropeine*, which contains a pyridine, but no benzene, residue, *phenylchloroacetyltropeine*, and *phenylaminoacetyltropeine* are all active in this respect, although less so than homatropine.

Fumaroyl-, tartryl-, cinnamoyl-, phthaloyl-, and *p*-hydroxybenzoyltropeines are inactive, but phenylcarbamo-, benzoyl-, phenylacetyl-*o*-, and *m*-hydroxybenzoyl-tropeines possess more or less marked mydriatic properties.

The above results were obtained by instillation of aqueous solutions, equivalent as regards tropine content with a 1 per cent. aqueous solution of homatropine hydrobromide, into the conjunctival sac of cats' eyes.

In conclusion, we have to thank Mr. H. H. Dale of the Wellcome Physiological Research Laboratories for carrying out the physiological examination of these tropeines, and Dr. P. Remfry for the preparation of phenylcarbamotropeine.

EXPERIMENTAL.

Atroglyceryltropeine, $OH\cdot CH_2\cdot CPh(OH)\cdot CO_2\cdot C_8H_{14}N$.

Twelve and a-half grams of atroglyceric acid and 10 grams of tropine were warmed together on the water-bath until a clear solution resulted, and this was heated to 120—125° in a stream of dry hydrogen chloride for four hours (Täuber, D.R.-P. 95853). The light brown gum was decomposed with ammonia and extracted with chloroform, from which the alkaloid was then extracted with 10 per cent. hydrochloric acid After regeneration with sodium carbonate and extraction with ether, the base was obtained as a viscid oil, which became crystalline on stirring with acetone. On recrystallisation from acetone, 3·1 grams of the pure tropeine were obtained, that is, 14 per cent. of the theoretical.

Atroglyceryltropeine crystallises from acetone or benzene in rectangular, oblong plates, which melt at 124—125° (corr.). It is very sparingly soluble in water or ether, sparingly so in acetone or benzene, but easily so in alcohol or ethyl acetate:

0·2022 gave 0·4945 CO_2 and 0·1363 H_2O. C = 66·7; H = 7·6.
0·3846 ,, 16·2 c.c. N_2 at 19° and 764 mm. N = 5·0.
$C_{17}H_{23}O_4N$ requires C = 66·8; H = 7·6; N = 4·6 per cent.

The *hydrobromide* crystallises from absolute alcohol or acetone in large, clear monoclinic plates, which melt at 144—145° (corr.). It is anhydrous and is easily soluble in water, fairly easily so in alcohol, and sparingly so in acetone:

0·1998 gave 0·0952 AgBr. Br = 20·3.
$C_{17}H_{23}O_4N,HBr$ requires Br = 20·7 per cent.

The *sulphate* crystallises from a mixture of absolute alcohol and ethyl acetate in fine matted needles, which melt at 163—164° (corr.). It is readily soluble in water or alcohol, and contains two and a-half molecular proportions of water of crystallisation:

0·1440 air-dried salt gave 0·2842 CO_2 and 0·0920 H_2O. C = 53·8; H = 7·2.
0·2396 ,, ,, ,, lost 0·0144 at 100°. H_2O = 6·0.
$(C_{17}H_{23}O_4N)_2,H_2SO_4,2\frac{1}{2}H_2O$ requires C = 54·2; H = 7·1; H_2O = 6·0 per cent.
0·1482 dried at 100° gave 0·0490 $BaSO_4$. SO_4 = 13·6.
$(C_{17}H_{23}O_4N)_2,H_2SO_4$ requires SO_4 = 13·6 per cent.

The *aurichloride* crystallises from dilute hydrochloric acid in clusters of golden, prismatic needles, which melt at 145—148° (corr.). It is sparingly soluble in water, but easily so in alcohol. It contains one-third of a molecular proportion of water of crystallisation:

0·2895 air-dried salt lost 0·0024 at 100°. H_2O = 0·8.
$C_{17}H_{23}O_4N,HAuCl_4,\frac{1}{3}H_2O$ requires H_2O = 0·9 per cent.
0·2871 dried at 100° gave 0·0874 Au. Au = 30·4.
$C_{17}H_{23}O_4N,HAuCl_4$ requires Au = 30·6 per cent.

The *picrate* crystallises from alcohol in fine yellow needles, which melt at 178—179° (corr.).

The *methobromide* is dimorphous; it separated from a solution of the base in absolute alcohol, to which methyl bromide had been added at 0°, in indefinite laminar crystals, which melted at 226—227°; on recrystallisation from absolute alcohol, it was obtained in radial clusters of prismatic needles, which melted at 218—219° (corr.); this melting point was unchanged by further crystallisation. It is readily soluble in water, but sparingly so in alcohol:

0·0842 gave 0·0392 AgBr. Br = 19·8.

$C_{17}H_{23}O_4N,CH_3Br$ requires Br = 20·0 per cent.

a-Hydroxy-β-phenylpropionyltropeine, $CH_2Ph\cdot CH(OH)\cdot CO_2\cdot C_8H_{14}N$.

Seven grams of α-hydroxy-β-phenylpropionic acid and 5 grams of tropine were heated for five hours at 130° in a stream of dry hydrogen chloride. The resulting gum was purified as in the case of atroglyceryltropeine, and gave a crude tropeine which crystallised on keeping. After recrystallisation from ether, 4·4 grams of the pure tropeine were obtained; the yield amounted to 43 per cent. of the theoretical.

a-Hydroxy-β-phenylpropionyltropeine is insoluble in water, but easily soluble in the other usual organic solvents. It crystallises from a concentrated ethereal solution in rosettes of needles, which melt at 89—90° (corr.):

0·1533 gave 0·3949 CO_2 and 0·1083 H_2O. C = 70·3; H = 7·9.

$C_{17}H_{23}O_3N$ requires C = 70·5; H = 8·0 per cent.

The *hydrobromide* crystallises from acetone in chisel-shaped needles, which melt at 173—175° (corr.). It is anhydrous, and is easily soluble in water, fairly easily so in alcohol, and sparingly so in acetone:

0·2325 gave 0·1195 AgBr. Br = 21·9.

$C_{17}H_{23}O_3N,HBr$ requires Br = 21·6 per cent.

The *sulphate* crystallises from a mixture of absolute alcohol and acetone in short, prismatic needles, which melt at 192—193° (corr.). It contains 2 molecules of water of crystallisation, and is easily soluble in water or alcohol, but sparingly so in acetone:

0·2068 air-dried salt lost 0·0108 at 110°. H_2O = 5·2.

$(C_{17}H_{23}O_3N)_2,H_2SO_4,2H_2O$ requires H_2O = 5·1 per cent.

0·1912 dried at 110° gave 0·0674 $BaSO_4$. SO_4 = 14·5.

$(C_{17}H_{23}O_3N)_2,H_2SO_4$ requires SO_4 = 14·2 per cent.

The *aurichloride* crystallises from alcohol in hard, yellow plates, which melt at 188—189° (corr.). It is anhydrous, and is insoluble in water, but sparingly soluble in cold alcohol:

0·1720 gave 0·0536 Au. Au = 31·2.

$C_{17}H_{23}O_3N,HAuCl_4$ requires Au = 31·3 per cent.

The *picrate* crystallises from alcohol in short, yellow needles, which melt at 159—160° (corr.).

The *methobromide* crystallises from absolute alcohol in scales, which melt at 213—215° (corr.). It is easily soluble in water or alcohol:

0·1606 gave 0·0785 AgBr. Br = 20·8.

$C_{17}H_{23}O_3N,CH_3Br$ requires Br = 20·8 per cent.

α-Hydroxy-β-2-pyridylpropionyltropeine, $C_5NH_4\cdot CH_2\cdot CH(OH)\cdot CO_2\cdot C_8H_{14}N$.

Fourteen grams of α-hydroxy-β-2-pyridylpropionic acid and 10 grams of tropine were subjected to the action of a stream of dry hydrogen chloride at 130—135° for seven hours. The resulting gum was worked up in the usual manner, and gave 5 grams of a light brown syrup, which readily formed crystalline salts; the yield amounted to 24 per cent. of the theoretical.

This base was not obtained in a crystalline form even after regeneration from a pure salt.

The *sulphate* crystallises from a mixture of absolute alcohol and acetone in clusters of prismatic needles, which melt at 152—154° (corr.). It is very deliquescent, and is easily soluble in water or alcohol, giving a neutral solution:

0·1526 dried at 100° gave 0·3165 CO_2 and 0·0941 H_2O. C = 56·6; H = 6·9.
0·1805 dried at 100° gave 0·0640 $BaSO_4$. SO_4 = 14·6.
$(C_{16}H_{22}O_3N_2)_2,H_2SO_4$ requires C = 56·5; H = 6·9; SO_4 = 14·2 per cent.

The *dihydrochloride* crystallises from absolute alcohol in highly refracting, colourless prisms, which sinter at 205° and melt and decompose at 208—210° (corr.). It is deliquescent and easily soluble in water, giving an acid solution, but is sparingly soluble in cold absolute alcohol:

0·1506 dried at 100° gave 0·2923 CO_2 and 0·0913 H_2O. C = 52·9; H = 6·8.
0·1834 „ „ „ 0·1459 AgCl. Cl = 19·7.
$C_{16}H_{22}O_3N_2,2HCl$ requires C = 52·9; H = 6·7; Cl = 19·5 per cent.

The *diaurichloride* crystallises from alcohol in circular grains, which effervesce at 223° (corr.) after beginning to decompose a few degrees below this temperature. It contains $1\frac{1}{2}$ molecular proportions of water of crystallisation, and is very sparingly soluble in water or alcohol:

0·2800 air-dried salt lost 0·0077 at 100°. H_2O = 2·7.
$C_{16}H_{22}O_3N_2,2HAuCl_4,1\frac{1}{2}H_2O$ requires H_2O = 2·7 per cent.
0·2723 dried at 100° gave 0·1108 Au. Au = 40·7.
$C_{16}H_{22}O_3N_2,2HAuCl_4$ requires Au = 40·4 per cent.

Phenylchloroacetyltropeine, $C_6H_5\cdot CHCl\cdot CO_2\cdot C_8H_{14}N$.

Twenty-five grams of phenylchloroacetyl chloride and 24 grams of tropine hydrochloride were heated together for two hours on the water-bath. The product was worked up in the usual manner, and the crude tropeine dissolved in acetone and neutralised with hydrochloric acid; 35 grams of pure phenylchloroacetyltropeine hydrochloride crystallised out, that is, 78 per cent. of the theoretical.

The base was obtained as a viscous oil, which became granular when stirred with light petroleum, and proved to be very deliquescent.

The *hydrochloride* crystallises from acetone in short, glistening needles, which melt at 205—206° (corr.). It is anhydrous, and is easily soluble in water or alcohol, but sparingly so in acetone:

0·1610 gave 0·3440 CO_2 and 0·0926 H_2O. C = 58·3; H = 6·4.
0·1960 ,, (by Carius' method) 0·1706 AgCl. Cl = 21·5.
$C_{16}H_{20}O_2NCl,HCl$ requires C = 58·2; H = 6·4; Cl = 21·5 per cent.

The *aurichloride* crystallises from absolute alcohol in large, irregular, golden grains, which melt at 148—149° (corr.). It is anhydrous, and is very sparingly soluble in cold water or alcohol:

0·3112 gave 0·0970 Au. Au = 31·2.
$C_{16}H_{20}O_2NCl,HAuCl_4$ requires Au = 31·1 per cent.

The *picrate* crystallises from absolute alcohol in radial clusters of feathery needles, which melt at 203—204° (corr.).

The *methobromide* separates from absolute alcohol as a microcrystalline powder, which decomposes at 240—242° (corr.). It is easily soluble in water, but sparingly so in cold alcohol:

0·1723 air-dried salt gave 0·3339 CO_2 and 0·0918 H_2O. C = 52·9; H = 6·0.
$C_{16}H_{20}O_2NCl,CH_3Br$ requires C = 52·5; H = 6·0 per cent.

Phenylaminoacetyltropeine, $C_6H_5{\cdot}CH(NH_2){\cdot}CO_2{\cdot}C_8H_{14}N$.

Twelve grams of phenylaminoacetic acid and 10 grams of tropine were subjected to the action of dry hydrogen chloride for twelve hours at 130—135°. The crude base, which was isolated in the usual manner, was converted into the hydrobromide, and this salt was crystallised from absolute alcohol. The yield of hydrobromide was 4 grams, that is, 13 per cent. of the theoretical.

The base did not crystallise.

The *dihydrobromide* crystallises from absolute alcohol in clusters of short needles, which melt at 199° (corr.) to a viscous liquid. It is very deliquescent and easily soluble in water, giving an acid solution, but sparingly so in cold absolute alcohol:

0·1874 dried at 100° gave 0·3070 CO_2 and 0·0990 H_2O. C = 44·7; H = 5·9.
0·1663 ,, ,, ,, 0·1430 AgBr. Br = 36·6.
$C_{16}H_{22}O_2N_2,2HBr$ requires C = 44·0; H = 5·6; Br = 36·7 per cent.

The *dipicrate* crystallises from absolute alcohol in microscopic needles, which decompose at 231° (corr.):

0·1832 gave 0·3084 CO_2 and 0·0646 H_2O. C = 45·9; H = 4·0.
$C_{16}H_{22}O_2N_2,2C_6H_3O_7N_3$ requires C = 45·9; H = 3·9 per cent.

Fumaroyltropeine, $C_8H_{14}N\cdot CO_2\cdot CH\colon CH\cdot CO_2\cdot C_8H_{14}N$.

Six grams of malic acid and 10 grams of tropine were subjected to the action of a stream of dry hydrogen chloride for eight hours at 130—135°. The resulting gum was worked up in the usual manner, and the crude tropeine rendered crystalline by stirring with acetone. The yield amounted to 1·4 grams, that is, 11 per cent. of the theoretical.

Fumaroyltropeine crystallises from acetone in large, monoclinic scales, which melt at 165—166° (corr.). It is very sparingly soluble in water or cold acetone, but easily so in alcohol:

0·1345 gave 0·3268 CO_2 and 0·1049 H_2O. C = 66·3; H = 8·8.
$C_{20}H_{30}O_4N_2$ requires C = 66·2; H = 8·4 per cent.

The *hydrochloride* crystallises from aqueous acetone in glistening plates, which do not decompose at 310° (corr.). It contains 2 molecules of water of crystallisation, and is easily soluble in water, but very sparingly so in absolute alcohol:

0·1811 air-dried salt lost 0·0138 at 120°. H_2O = 7·6.
$C_{20}H_{30}O_4N_2,2HCl,2H_2O$ requires H_2O = 7·6 per cent.
0·1673 dried at 120° gave 0·1099 AgCl. Cl = 16·2.
$C_{20}H_{30}O_4N_2,2HCl$ requires Cl = 16·3 per cent.

The *hydriodide* crystallises from water in hard clusters of plates, which melt at 283—285° (corr.). It contains 2 molecules of water of crystallisation, and is moderately easily soluble in water, but sparingly so in alcohol:

0·1858 air-dried salt lost 0·0100 at 100°. H_2O = 5·4.
$C_{20}H_{30}O_4N_2,2HI,2H_2O$ requires H_2O = 5·5 per cent.
0·1758 dried at 100° gave 0·1331 AgI. I = 40·9.
$C_{20}H_{30}O_4N_2,2HI$ requires I = 41·1 per cent.

Tartryltropeine.[*]

Seven grams of tartaric acid and 10 grams of tropine were subjected to a stream of dry hydrogen chloride for eight hours at 130—135°. The resulting gum was worked up in the usual manner, and the crude base, on stirring with acetone, gave 2·3 grams of the pure tropeine, that is, 16 per cent. of the theoretical.

Tartryltropeine crystallises from absolute alcohol in glistening prisms, which melt at 223—224° (corr.); it is somewhat sparingly soluble in water, and sparingly so in absolute alcohol:

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[*] Merck, *Chem Centr.*, 1895, i, 434.

0·1534 gave 0·3388 CO_2 and 0·1124 H_2O. $C = 60·2$; $H = 8·2$.

$C_{20}H_{32}O_6N_2$ requires $C = 60·6$; $H = 8·2$ per cent.

The *hydrochloride* crystallises from absolute alcohol in microscopic, glistening needles, which contain 3 molecules of water of crystallisation. After drying at 100°, this salt decomposes at 273° (corr.). It is easily soluble in water or hot alcohol :

0·3509 lost 0·0345 at 100°. $H_2O = 9·8$.

$C_{20}H_{32}O_6N_2,2HCl,3H_2O$ requires $H_2O = 10·3$ per cent.

0 1664 dried at 100° gave 0·1017 AgCl. $Cl = 15·1$.

$C_{20}H_{32}O_6N_2,2HCl$ requires $Cl = 15·1$ per cent.

The *sulphate* is obtained in long needles by spontaneous evaporation of an aqueous solution. It contains one and a-half molecular proportions of water of crystallisation, and decomposes at 287° (corr.). It is easily soluble in water, but very sparingly so in hot alcohol :

0·2015 air-dried salt lost 0·0112 at 100°. $H_2O = 5·6$.

$C_{20}H_{32}O_6N_2,H_2SO_4,1\frac{1}{2}H_2O$ requires $H_2O = 5·2$ per cent.

0·1911 dried at 100° gave 0·0927 $BaSO_4$. $SO_4 = 20·0$.

$C_{20}H_{32}O_6N_2,H_2SO_4$ requires $SO_4 = 19·4$ per cent.

The *picrate* crystallises from boiling water in round, yellow grains, which begin to turn brown at about 270°, and effervesce at 287° (corr.).

Phenylcarbamotropeine.

This base was prepared by the method given by Petit and Polonowski (*Bull. Soc. chim.*, 1893, [iii], 9, 1017) ; it melted at 171—172° (corr.) : Petit and Polonowski give 170°.

The *sulphate* crystallises from water in radiating clusters of prismatic needles, which melt and decompose at 201° (corr.). It contains 4 molecules of water of crystallisation :

0·2244 air-dried salt lost 0·0229 at 100°. $H_2O = 10·2$.

$(C_{15}H_{20}O_2N_2)_2,H_2SO_4,4H_2O$ requires $H_2O = 10·4$ per cent.

0·1976 dried at 100° gave 0·0758 $BaSO_4$. $SO_4 = 15·8$.

$(C_{15}H_{20}O_2N_2)_2,H_2SO_4$ requires $SO_4 = 15·5$ per cent.

The *hydrochloride* crystallises from aqueous alcohol in large, rectangular plates, which melt at 289—290° (corr.) and are anhydrous :

0·2160 air-dried salt gave 0·1036 AgCl. $Cl = 11·9$.

$C_{15}H_{20}O_2N_2,HCl$ requires $Cl = 11·9$ per cent.

The *aurichloride* crystallises from water as an orange-red, crystalline powder, which melts at 188—189° (corr.) :

0·1906 air-dried salt gave 0·0627 Au. $Au = 32·9$.

$C_{15}H_{20}O_2N_2,HAuCl_4$ requires $Au = 32·8$ per cent.

The *picrate* crystallises from aqueous alcohol in glistening, yellow, monoclinic plates, which melt at 223—224° (corr.).

*Benzoyltropeine.**

This base was prepared by heating together benzoyl chloride and tropine hydrochloride for three hours on the water-bath; the yield of pure hydrochloride amounted to 77 per cent. of the theoretical. The base was obtained by the action of sodium carbonate on an aqueous solution of the hydrochloride, and formed glistening plates, which melted at 58° (corr.), as stated by Ladenburg.

The *hydrochloride* crystallises from absolute alcohol in highly-refracting prisms, which melt at 275° (corr.). It is anhydrous, and is easily soluble in water, but sparingly so in absolute alcohol:

0·1641 gave 0·3835 CO_2 and 0·1048 H_2O. C = 63·7; H = 7·2.
0·1502 ,, 0·0764 AgCl. Cl = 12·6.

$C_{15}H_{19}O_2N,HCl$ requires C = 63·9; H = 7·2; Cl = 12·6 per cent.

The aurichloride crystallises from absolute alcohol in yellow, monoclinic plates, which melt at 190—192° (corr.). It is anhydrous, and is insoluble in water, but sparingly so in cold alcohol:

0·2253 gave 0·0758 Au. Au = 33·6.

$C_{15}H_{19}O_2N,HAuCl_4$ requires Au = 33·7 per cent.

The picrate melts at 252—255° (corr.).

Phenylacetyltropeine.

This base was prepared by heating together on the water-bath phenylacetyl chloride and tropine hydrochloride; the yield of pure product amounted to 40 per cent. of the theoretical.

The base was precipitated as an oil on the addition of aqueous sodium carbonate to a solution of the sulphate, and did not crystallise on long standing in a vacuum desiccator over sulphuric acid.

The sulphate crystallises from acetone in glistening leaflets, which appear under the microscope to be well-defined, monoclinic plates. It melts at 107—108° (corr.), and contains two and a-half molecular proportions of water of crystallisation. This salt is easily soluble in water and alcohol, but sparingly so in cold acetone:

0·2675 air-dried salt lost 0·0186 at 100°. H_2O = 7·0.

$(C_{16}H_{21}O_2N)_2,H_2SO_4,2\frac{1}{2}H_2O$ requires H_2O = 6·8 per cent.

0·1762 dried at 100° gave 0·4043 CO_2 and 0·1139 H_2O. C = 62·6; H = 7·2.

0·1914 dried at 100° gave 0·0722 $BaSO_4$. SO_4 = 15·5.

$(C_{16}H_{21}O_2N)_2,H_2SO_4$ requires C = 62·3; H = 7·2; SO_4 = 15·6 per cent.

The aurichloride crystallises from absolute alcohol in monoclinic, hexagonal plates, which begin to sinter at 167° and melt at 179° (corr.). It is anhydrous, and is sparingly soluble in water and alcohol.

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* This tropeine and those following it have been described by Ladenburg, *Annalen*, 1883, **217**, 82.

The *picrate* crystallises from alcohol in hard, yellow, glistening prisms, which melt at 170—171° (corr.).

Cinnamoyltropeine.

This compound was obtained in a yield of 74 per cent. of the theoretical by heating together equimolecular proportions of cinnamoyl chloride and tropine hydrochloride. It was also obtained in a yield of 40 per cent. of the theoretical by passing a stream of dry hydrogen chloride through tropine β-hydroxy-β-phenylpropionate at 125°.

The base is obtained in glistening leaflets, melting at 45—46° (corr.), on the addition of aqueous sodium carbonate to a solution of a soluble salt, and crystallises from light petroleum in long, flat needles, which melt at the same temperature and contain one molecule of water of crystallisation. The water is readily removed in a vacuum over sulphuric acid, and the anhydrous base then melts at 36—37° (corr.).* It is insoluble in water, but easily soluble in the usual organic solvents:

0·1104 air-dried substance gave 0·2846 CO_2 and 0·0758 H_2O. C = 70·3; H = 7·7.

0·5555 air-dried substance lost 0·0324 in a vacuum over H_2SO_4. H_2O = 5·8.

$C_{17}H_{21}O_2N,H_2O$ requires C = 70·5; H = 8·0; H_2O = 6·2 per cent.

0·1526, dried in a desiccator, gave 0·4205 CO_2 and 0·1063 H_2O. C = 75·1; H = 7·8.

$C_{17}H_{21}O_2N$ requires C = 75·2; H = 7·8 per cent.

The hydrochloride crystallises from either water or ethyl acetate in long, white needles, which melt and decompose at 272° (corr.). It contains rather more than 1½ molecular proportions of water of crystallisation, and is somewhat sparingly soluble in water or ethyl acetate, but easily so in alcohol:

0·2081 air-dried salt lost 0·0190 at 100°. H_2O = 9·1.

$C_{17}H_{21}O_2N,HCl,1\frac{1}{2}H_2O$ requires H_2O = 8·1 per cent.

0·1510 dried at 100° gave 0·0689 AgCl. Cl = 11·3.

$C_{17}H_{21}O_2N,HCl$ requires Cl = 11·5 per cent.

The *hydrobromide* crystallises from ethyl acetate in long, glistening needles, which melt at 254—255° (corr.). It contains a somewhat variable proportion of water of crystallisation, representing about

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* Ladenburg has described this base as small leaflets, which melt at 70° and are anhydrous.

$1\frac{1}{2}$ molecular proportions, and is sparingly soluble in water or ethyl acetate:

0·2161 air-dried salt lost 0·0139 at 100°. $H_2O = 6·4$.
0·3743 ,, ,, ,, ,, 0·0295 ,, 100°. $H_2O = 7·9$.
$C_{17}H_{21}O_2N,HBr,1\frac{1}{2}H_2O$ requires $H_2O = 7·1$ per cent.
0·1511 dried at 100° gave 0·3222 CO_2 and 0·0843 H_2O. C = 58·1; H = 6·2.
0·2022 dried at 100° gave 0·1066 AgBr. Br = 22·4.
$C_{17}H_{21}O_2N,HBr$ requires C = 57·9; H = 6·3; Br = 22·7 per cent.

The *sulphate* crystallises from ethyl acetate in irregular plates, which melt at 227—229° (corr.). It contains 5 molecules of water of crystallisation, and is moderately easily soluble in water:

0·3207 air-dried salt lost 0·0394 at 100°. $H_2O = 12·3$.
$(C_{17}H_{21}O_2N)_2,H_2SO_4,5H_2O$ requires $H_2O = 12·3$ per cent.
0·1890 dried at 100° gave 0·0698 $BaSO_4$. $SO_4 = 15·2$.
$(C_{17}H_{21}O_2N)_2,H_2SO_4$ requires $SO_4 = 15·0$ per cent.

The aurichloride crystallises from alcohol in fern-like clusters of yellow plates, which melt at 174—175° (corr.).

The *picrate* crystallises from alcohol in short, yellow needles, which melt at 244—245° (corr.).

The *methobromide* crystallises from ethyl acetate in glistening leaflets, which melt and decompose at 288—291° (corr.). It is anhydrous, and is very easily soluble in water, but sparingly so in alcohol:

0·2019 gave 0·1041 AgBr. Br = 21·9.
$C_{17}H_{21}O_2N,CH_3Br$ requires Br = 21·8 per cent.

Phthaloyltropeine.

This compound was prepared by heating together at 130°, for three hours, one molecule of phthaloyl chloride and two molecules of tropine hydrochloride; the yield of pure product, weighed as sulphate, amounted to about 40 per cent. of the theoretical.

The base crystallises from ether in fine, glistening needles, which melt at 67—68° (corr.).*

The *sulphate* is obtained on the addition of acetone to an absolute alcoholic solution in short, glistening needles, which decompose at 160—165° (corr.). It is deliquescent, and very easily soluble in water or alcohol:

0·1375 dried at 100° gave 0·2838 CO_2 and 0·0810 H_2O. C = 56·3; H = 6·6.

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* Ladenburg gives m. p. 70°.

0·2035 dried at 100° gave 0·0951 $BaSO_4$. $SO_4 = 19·2$.

$C_{24}H_{32}O_4N_2,H_2SO_4$ requires $C = 56·4$; $H = 6·7$; $SO_4 = 18·8$ per cent.

The *hydriodide* crystallises from water in long needles, which contain 4 molecules of water of crystallisation. After drying at 100°, this salt commences to sinter at about 205° (corr.) and gradually becomes transparent. It is somewhat sparingly soluble in water and sparingly so in alcohol:

0·2898 air-dried salt lost 0·0273 at 100°. $H_2O = 9·4$.

$C_{24}H_{32}O_4N_2,2HI,4H_2O$ requires $H_2O = 9·7$ per cent.

0·2625 dried at 100° gave 0·1822 AgI. $I = 37·5$.

$C_{24}H_{32}O_4N_2,2HI$ requires $I = 38·0$ per cent.

The *aurichloride* crystallises from dilute alcohol in long, diamond-shaped plates, which contain 3 molecules of water of crystallisation and melt at 110—113° (corr.); it is sparingly soluble in water or absolute alcohol, but more easily so in dilute alcohol:

0·2921 air-dried salt lost 0·0136 at 110°. $H_2O = 4·7$.

$C_{24}H_{32}O_4N_2,2HAuCl_4,3H_2O$ requires $H_2O = 4·7$ per cent.

0·2785 dried at 110° gave 0·1011 Au. $Au = 36·3$.

$C_{24}H_{32}O_4N_2,2HAuCl_4$ requires $Au = 36·1$ per cent.

o-*Hydroxybenzoyltropeine.*

This base was prepared by passing dry hydrogen chloride through tropine salicylate for fifteen hours at 130—135°; the yield of pure base amounted to 16 per cent. of the theoretical.

o-Hydroxybenzoyltropeine melts at 61—63° (corr.): *

The hydrochloride crystallises from absolute alcohol in prismatic needles, which melt at 267° (corr.) and contain half a molecular proportion of water of crystallisation. It is easily soluble in water,† but somewhat sparingly so in alcohol:

0·2133 air-dried salt lost 0·0058 at 100°. $H_2O = 2·7$.

$C_{15}H_{19}O_3N,HCl,\frac{1}{2}H_2O$ requires $H_2O = 2·9$ per cent.

0·2065 dried at 100° gave 0·0968 AgCl. $Cl = 11·6$.

$C_{15}H_{19}O_3N,HCl$ requires $Cl = 11·9$ per cent.

The *hydrogen sulphate* crystallises from absolute alcohol in prismatic needles, which melt at 254° (corr.). It is anhydrous, and is easily soluble in water, but sparingly so in alcohol:

0·1528 gave 0·2804 CO_2 and 0·0832 H_2O. $C = 50·1$; $H = 6·1$

0·1582 „ 0·1040 $BaSO_4$. $SO_4 = 27·0$.

$C_{15}H_{19}O_3N,H_2SO_4$ requires $C = 50·1$; $H = 5·9$; $SO_4 = 26·7$ per cent.

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* Ladenburg gives 58—60°.

† Ladenburg states that this salt is not easily soluble in water.

The aurichloride crystallises from dilute alcohol in golden needles, which decompose at 222° (corr.).

m-*Hydroxybenzoyltropeine.*

This base was prepared by passing dry hydrogen chloride through tropine *m*-hydroxybenzoate for eight hours at 130—135°; the yield of pure base amounted to 43 per cent. of the theoretical.

The base melts at 233—234° (corr.).*

The hydrochloride crystallises from absolute alcohol in prismatic needles, which decompose at 304° (corr.).

The *hydriodide* crystallises from water in long, stout needles, which melt and decompose at 248° (corr.), but begin to sinter at 244°. It is anhydrous, and is sparingly soluble in cold water or alcohol:

0·1418 gave 0·2412 CO_2 and 0·0658 H_2O. C = 46·4; H = 5·2.
0·1560 „ 0·0937 AgI. I = 32·5.
$C_{15}H_{19}O_3N,HI$ requires C = 46·3; H = 5·2; I = 32·6 per cent.

p-*Hydroxybenzoyltropeine.*

This base was prepared by passing dry hydrogen chloride through tropine *p*-hydroxybenzoate for four hours at 130—135°; the yield of pure base amounted to 28 per cent. of the theoretical.

The base crystallises from absolute alcohol in clusters of plates, which melt and decompose at 232—233° (corr.).†

The hydrochloride crystallises from water in monoclinic plates, which decompose at 315° (corr.). It is anhydrous, and moderately easily soluble in water, but sparingly so in absolute alcohol:

0·1529 gave 0·3395 CO_2 and 0·0920 H_2O. C = 60·5; H = 6·7.
0·1606 „ 0·0778 AgCl. Cl = 12·0.
$C_{15}H_{19}O_3N,HCl$ requires C = 60·5; H = 6·8; Cl = 11·9 per cent.

The *aurichloride* crystallises from dilute alcohol in clusters of yellow plates, which decompose at 222° (corr.). It is very sparingly soluble in water, but moderately easily so in dilute alcohol:

0·2526 gave 0·0825 Au. Au = 32·7.
$C_{15}H_{19}O_3N,HAuCl_4$ requires Au = 32·8 per cent.

The picrate crystallises from alcohol in yellow, monoclinic leaflets, which melt at 235—237° (corr.).

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* Ladenburg gives m. p. 226°.

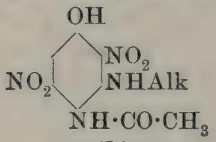
† Ladenburg gives m. p. 227°.

CXVII.—*Syntheses with Phenol Derivatives containing a Mobile Nitro-group. Part II. The Interaction of 2 : 3 : 5-Trinitro-4-acetylaminophenol and Amines (continued).*

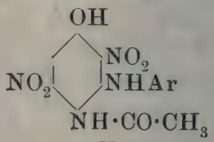
By RAPHAEL MELDOLA, F.R.S., and JAMES GORDON HAY, A.I.C.

IT was shown in our last communication on this subject (Trans., 1908, **93**, 1659) that the above trinitro-compound readily undergoes condensation with primary amines with the formation of catenation products of the nature of substituted diarylamines, which then give rise to iminazoles by the usual process of ring formation. As trinitroacetylaminophenol is the most readily prepared of the various polynitro-compounds containing a mobile nitro-group, we have continued our experiments with this substance, with the object of ascertaining whether the reaction is a perfectly general one, or whether the character and position of the substituents in the aromatic nucleus of the primary amine influences the rate of decomposition as determined by the yield of iminazole in a given time. The amines formerly employed, namely, the chloroanilines, nitroanilines, anisidines, and the homologues of aniline, made it evident that the substituents, Cl, NO_2, $O{\cdot}CH_3$, CH_3, exerted no retarding influence when in the meta- or para-position, but that in the ortho-position a marked protective (steric) influence was manifest, the inhibition in the case of the nitro-group being absolute. The extension of the research to other substituted primary amines has confirmed this conclusion, and has also revealed the fact that basic substituents, such as NH_2, $N(CH_3)_2$, etc., act very unfavourably. Thus, good results have been obtained with the bromoanilines, aminophenols, aminobenzoic acids, acetyl-*p*-phenylenediamine, sulphanilic acid, and *p*-aminoacetophenone. Where sets of isomerides have been studied quantitatively, the steric hindrance exerted by the ortho-substituent has again become evident, as shown by the tables given below. No iminazole formation has been observed with *m*- and *p*-phenylenediamine or with dimethyl-*p*-phenylenediamine. Thus the substituents, Br, OH, CO_2H, NHAc, SO_3H, $CO{\cdot}CH_3$, belong to the same category as those contained in the amines previously investigated, the production of iminazoles taking place readily when the substituents are in the meta- or para-position, and less readily when in the ortho-position. The negative results with amines containing a basic substituent are of special interest; the trinitro-compound is readily decomposed by these amines with the elimination of the nitro-group, but no catenation occurs, and neither diarylamines nor iminazoles are formed. The ortho-diamines have not yet been investigated, as it is not unlikely that in these cases the reaction may take a different course. In the case of heteronucleal basic substituents the deterrent action of the substituent is not so marked, since benzidine and tolidine give definite products, although the yield is not very good. Aminoazobenzene does not form an iminazole under the usual conditions.

A general comparison of the results obtained in this and the previous papers (Trans., 1906, **89**, 1935; also the last paper referred to above) brings out the fact that mixed arylalkylamines of type I are less ready to "anhydridise" than diarylamines of type II.



(I.)



(II.)

This is shown by the circumstance that when such amines as ethylamine or benzylamine react with the trinitro-compound, the intermediate product can be isolated, whereas aromatic amines pass at once and to a preponderating extent into the iminazole stage. That the velocity of iminazole formation is dependent on the nature and not on the weight of the radicle attached to the NH_2-group is proved by the similar behaviour of ethyl and benzyl having the relative weights 29 and 91.

The "protecting" influence of the substituents shown by the sets of isomerides given in the subjoined tables has been determined quantitatively by the method described in our last paper. It is unnecessary to repeat the description of this method here, although each set of crude iminazoles has required special treatment in order to estimate the actual quantity of the pure iminazole formed. The details of purification are given in the experimental part. Only those sets are now given which we have proved to our satisfaction to give dependable quantitative results. Although several other amines than those specified below have been included in our experiments, we do not attach the same weight to the results from the quantitative standpoint on account of the difficulty of separating the iminazole from the associated secondary products. For the sake of comparison we again give Wedekind's results with picryl chloride so far as this investigator's experiments have been extended to the same amines as those employed by us. The numbers, as before, indicate the percentage of yield calculated with reference to that theoretically obtainable.

	Bromoanilines.	Chloroanilines.
Ortho : (I) 87·9 ; (II) 88·4. Mean (corrected for solubility and anhydridisation),	88·15	79·0
Meta : (I) 90·2 ; (II) 90·1. Mean (corrected for solubility and anhydridisation),	90·15	80·6
Para : (I) 91·3 ; (II) 95·1. Mean (corrected for solubility and anhydridisation),	93·2	88·74

Wedekind does not appear to have studied the interaction of picryl chloride and the bromoanilines. The most interesting and possibly important result brought out by this series of determinations is that in the same time, the bromoanilines, while preserving the same order, give a better yield than the corresponding chloroanilines, the numbers for which are taken from our last paper and given for comparison. We are inclined to attribute this result to the more strongly negative character of the chlorine atom, but further experiments will be necessary to establish this point. The results as they stand indicate that the weight (or size) of the halogen atom is not the cause of the protecting influence in the ortho-position, since the heavier atom, bromine, affords less protection than chlorine.

Aminobenzoic Acids.

	A.	*B.*	Wedekind.
Ortho : (I) 89·1 ; (II) 87·8 ; (III) 86·2. Mean (corrected for solubility and anhydridisation)	87·7	72·0	84·7
Meta : (I) 107·6 ; (II) 105·1 ; (III) 106·2. Mean (corrected for solubility and anhydridisation)	106·3	101·9	84·7
Para : (I) 108·6 ; (II) 109·3 ; (III) 108·2. Mean (corrected for solubility and anhydridisation)	108·7	103·9	97·9

In this series much difficulty was experienced in finding a suitable method of purification. The secondary products are, like the iminazoles, phenolic (acidic) in character, and therefore not completely removed by the alkaline treatment, a fact which accounts for the yield being higher in the case of the meta- and para-compounds than that required by theory. The numbers, although high, are, however, fairly comparable among themselves (*A*). Another series (*B*) gives the yields obtained after the alkaline treatment, followed by the precipitation of the iminazole as a silver salt, the latter being dried and weighed. Although the yields are less by this method, the same order is retained.

Aminophenols.

		W.
Ortho : (I) 86·8 ; (II) 86·5. Mean (corrected for solubility, anhydridisation, and by sulphonation)	58·03	
Meta : (I) 94·9 ; (II) 99·5. Mean (corrected for solubility, anhydridisation, and for loss of weight on sulphonation)	94·4	86—88
Para : (I) 57·6 ; (II) 59·3 ; (III) 60·8 ; (IV) 60·2. Mean (corrected for solubility, anhydridisation, and for loss of weight on sulphonation)..	55·8	97—98

In this series the alkaline treatment leaves practically no residue, the whole product being phenolic. It was found that by heating with concentrated sulphuric acid all these iminazoles could be sulphonated, the impurities being thus removed. In the case of the ortho-compound, the crystalline sulphonic acid was collected and weighed, and the yield calculated from the weight of acid after correcting for the solubility of the latter. In the case of the meta- and para-compounds, the impurity was collected and weighed directly, as the sulphonic acids were too soluble to be dealt with for quantitative purposes.

Naphthylamines.

		W.
α: (I) 98·3; (II) 98·3.		
Mean (corrected for solubility and anhydridisation)	98·3	Almost quantitative
β: (I) 98·2; (II) 99·8.		
Mean (corrected for solubility and anhydridisation)	99·0	Not given

The chief point of interest brought out by these and the previously-published quantitative results is that in amines containing the groups $O\cdot CH_3$ and OH the para-position of the substituent is also unfavourable to catenation, the degree of inhibition in the case of the hydroxyl group being even greater for the para- than for the ortho-position. It is evident that in these cases some influence other than "steric hindrance" determines the rate of condensation, and that the mobile nitro-group has a specific action differing from that of the chlorine atom of picryl chloride. This appears from a comparison of our results with Wedekind's, which are normal from the "steric" point of view for all the isomeric amines investigated by him with the exception of the nitroanilines, in which series he finds that the meta-compound gives the highest yield.

The results of all the determinations are summarised below, the prefixes *o*, *m*, and *p* indicating the isomeride being placed in the ascending order of yield:

	Trinitroacetyl-aminophenol.	Picryl chloride.
Chloroanilines	*o- m- p-*	*o- m- p-*
Bromoanilines	*o- m- p-*	—
Nitroanilines	*o- m- p-*	*o- p- m-*
Aminophenols	*p- o- m-*	(?) *m- p-*
Anisidines	*o- p- m-*	—
Aminobenzoic acids	*o- m- p-*	{*o- m-*} *p-*

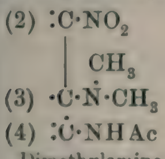
According to Menschutkin (*Ber.*, 1897, **30**, 2775, 2966; *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 444), allyl bromide reacts with the chloroanilines in the same order, namely, *o* (9), *m* (23), *p* (34). Although, as stated in our last paper, the substituted amines containing the CH_3-group, that is, the homologues of aniline, do not give such definite quantitative results as those containing acid radicles, the following average numbers previously obtained for *o*- and *p*-toluidine compared with that now obtained for mesidine bring out the influence of the position of the CH_3-group very clearly. The numbers given by ψ-cumidine are unfortunately too irregular to be included :

o-Toluidine (71—72) ; *p*-Toluidine (87—88) ; Mesidine, (50).

Experiments with Secondary Amines with reference to Steric Hindrance.

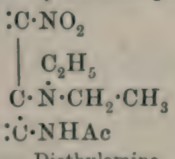
Our object in extending the research in this direction was primarily to ascertain whether the length of the chain of atoms influenced the rate of catenation, as might have been expected from Bischoff's "dynamic hypothesis" (Trans., 1908, **93**, 1665). We had previously found that dimethylamine and piperidine gave positive results, while methylaniline, diphenylamine, benzylaniline, and carbazole were without action under any conditions. A continuation of the experiments with the homologues of dimethylamine has revealed the unexpected fact that these also are without action on the trinitro-compound under any conditions. With dimethylamine and piperidine the reaction takes place quite readily, and with excellent yields when the materials are simply boiled together in alcoholic solution in the usual way. No condensation takes place with diethylamine, dipropylamine, di*iso*butylamine, or diamylamine, either in alcoholic solution or when the trinitro-compound is heated with an excess of the dialkylamine without any diluent. Under no conditions is there any action beyond the formation of a salt, or, if the solution is overheated, complete decomposition of the trinitro-compound. On the other hand, when catenation does take place, as with dimethylamine and piperidine, the products are definite and extremely stable.

The negative results given by all the homologous dialkylamines above dimethylamine suggest an interesting extension of the ordinary "steric" hypothesis. Taking from the benzene nucleus of the trinitro-compound only the carbon atoms 2, 3, and 4, with their attached radicles which are concerned in the reactions under investigation, it will be seen that with diethylamine there is no reason to expect complete inhibition, since the longest chain contains four atoms, and does not therefore offer any critical position :



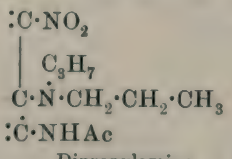
$$\begin{array}{ll} (2) & \vdots C\cdot NO_2 \\ & \;|\quad CH_3 \\ (3) & \cdot C\cdot \dot{N}\cdot CH_3 \\ (4) & \dot{\vdots}C\cdot NHAc \end{array}$$

Dimethylamine compound.
Chain : C·N·C (=3).



$$\begin{array}{l} \vdots C\cdot NO_2 \\ \;|\quad C_2H_5 \\ C\cdot \dot{N}\cdot CH_2\cdot CH_3 \\ \dot{\vdots}C\cdot NHAc \end{array}$$

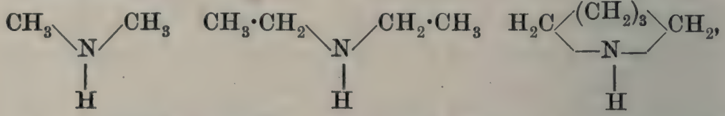
Diethylamine compound.
Chain : C·N·C·C (=4).



$$\begin{array}{l} \vdots C\cdot NO_2 \\ \;|\quad C_3H_7 \\ C\cdot \dot{N}\cdot CH_2\cdot CH_2\cdot CH_3 \\ \dot{\vdots}C\cdot NHAc \end{array}$$

Dipropylamine compound.
Chain : C·N·C·C·C (=5).

According to the current hypothesis, as shown by the above formulæ, the influence of steric hindrance should commence to make itself felt only from dipropylamine upwards. Since diethylamine is also without action, it may be suggested that it is the actual size of the radicles attached to the nitrogen atom which finally determine the process of catenation or its prevention. The mobile nitro-group (attached to C-atom No. 3) is already protected on both sides by the NO_2-group of No. 2 and the NHAc-group of No. 4. Any reacting molecule in order to be capable of coming within the sphere of influence of this nitro-group must therefore be of sufficient size to pass between the two protecting ortho-groups; if this size is exceeded, no action would take place. Thus, representing the nitrogen atom with its three bonds in one plane, an assumption in accordance with the known stereochemical character of this atom in its tervalent condition, the secondary amines:



may be supposed to present the critical minimum in the grouping $\mathrm{N}{<}^{\mathrm{C}}_{\mathrm{C}}$ of dimethylamine, which, by the addition of two carbon atoms on passing into the grouping $\mathrm{N}{<}^{\mathrm{C\cdot C}}_{\mathrm{C\cdot C}}$ of diethylamine, becomes too large to be effective. In piperidine the configuration must be supposed to be the same as in dimethylamine, hence its reactivity. This suggestion, although based on a purely mechanical conception, appears to account for the remarkable inertness of the higher secondary amines towards a compound of such great reactivity as trinitroacetylaminophenol. At any rate, as a working hypothesis, it may be found useful as a stimulus to further experimental work. We have not been able to find any close analogy with other compounds containing mobile radicles, but little work has as yet been done in this direction from this particular point of view. The results of Bischoff's experiments on catenation between the esters of the α-bromo-fatty acids and the amines (Stewart's *Stereochemistry*, pp. 364 *et seq.*) may perhaps be regarded as presenting a certain analogy to ours, since the mobile atom, Br, in this case is also protected by two neighbouring radicles:

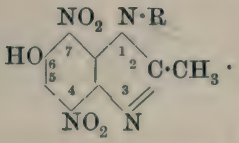
$$\begin{array}{l} \quad \mathrm{C}\colon\!(\mathrm{H\ and\ CH_3\ or\ C_2H_5}) \\ \mathrm{H\cdot\dot{C}\cdot Br} \\ \quad \mathrm{\dot{C}O\cdot O\cdot C_2H_5} \end{array}$$

It is noteworthy that the yield of catenation product diminishes considerably with secondary amines, more especially when the radicles associated with the nitrogen atom and the β-carbon atom are of a high order of complexity. With α-bromo*iso*valeric ester and secondary amines there is practically no reaction, excepting in the case of piperidine.

Wedekind's experiments with picryl chloride, as we have already pointed out,* are not strictly comparable with ours, as the extremely negative chlorine atom appears to be capable of overcoming steric protection in cases where the mobile nitro-group fails, as with methylaniline and benzylaniline. The velocity of the reaction between picryl chloride and secondary amines seems a promising subject of investigation from this point of view. The 2:3:4-trinitroanisole, recently described by Blanksma (*Chem. Weekblad*, 1909, 6, 85), contains a mobile nitro-group in position 3, but the interaction of this compound and secondary amines has not yet been studied.

EXPERIMENTAL.

No modification in the method of determining the yield of iminazole or in the process of forming the latter from the interacting materials has been found necessary. In the following description of the iminazoles prepared in the course of the present investigation, the atoms composing the iminazole ring have been numbered in the same order as before:



The Bromoaniline Series.

This series presented no special difficulties of manipulation, and the quantitative results were obtained quite readily, and, we believe, with great accuracy. Only in the case of the ortho-compound was there any considerable quantity of secondary product formed, but this was completely removed by two successive extractions with dilute sodium hydroxide solution in the way described in our previous paper (*loc. cit.*, p. 1669).

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* We stated in our last paper (*loc. cit.*, p. 1666, footnote) that Wedekind's materials were heated in sealed tubes to bring about catenation. On re-reading his paper we find, however, that his experiments were carried out in the same way as ours, namely, in alcoholic solution, under ordinary pressure, in a reflux apparatus. Our results, so far as concerns experimental conditions, are therefore comparable, excepting with regard to time, Wedekind stopping the reaction at the end of one hour. He does not state the quantity of solvent used.

Dinitrohydroxy-1-o-*bromophenylmethylbenziminazole.*

From the trinitro-compound and *o*-bromoaniline. After crystallisation from alcohol and glacial acetic acid, the compound consists of pale yellow needles of m. p. 184°. The crystals tend to retain acetic acid when this solvent is used, and must be well dried at 100° for analysis:

0·2466 gave 29·8 c.c. N_2 (moist) at 10° and 749·5 mm. N = 14·27.
$C_{14}H_9O_5N_4Br$ requires N = 14·25 per cent.

Dinitrohydroxy-1-m-*bromophenylmethylbenziminazole.*

Prepared as before from *m*-bromoaniline. The compound crystallises from acetic acid or from alcohol as an ochreous, microcrystalline powder; m. p. 211° with decomposition:

0·1870 gave 21·8 c.c. N_2 (moist) at 8·5° and 767·4 mm. N = 14·20.
$C_{14}H_9O_5N_4Br$ requires N = 14·25 per cent.

This compound is practically insoluble in cold water, and was recovered quantitatively from its alkaline solution on acidifying, so that no correction for solubility was required.

Dinitrohydroxy-1-p-*bromophenylmethylbenziminazole.*

From the trinitro-compound and *p*-bromoaniline. The compound is but sparingly soluble in alcohol, more readily in acetic acid. From alcohol it separates in lustrous, ochreous scales; m. p. (with decomposition) 248°:

0·1272 gave 15·2 c.c. N_2 (moist) at 12° and 762 mm. N = 14·22.
$C_{14}H_9O_5N_4Br$ requires N = 14·25 per cent.

This iminazole is also practically insoluble in water.

The Aminobenzoic Acid Series.

The secondary products formed in the synthesis of the iminazoles of this series are, as already stated, difficult to separate from the iminazoles, and several methods of purification were tried before satisfactory quantitative results could be obtained. As all these iminazoles crystallise well from alcohol and from acetic acid, attempts were made to separate the pure iminazole by crystallisation from these solvents. The weight of the iminazole thus obtained showed, however, such a serious loss in all cases as compared with the total weight of crude product obtained after the alkaline treatment, that it was evident that the loss was due, not to mere solubility in the pure solvent, but to solubility of the iminazole in a solution of the secondary product in alcohol or acetic acid. The method of purification by crystallisation was therefore abandoned for quantitative purposes, and the ordinary alkaline treatment adopted. As the yields thus obtained were somewhat higher than theoretically admissible, experiments were made with the object of finding some salt sufficiently insoluble to be precipitated from an aqueous solution. The silver salts, prepared as described below, were found suitable for this purpose, and the corrected results thus obtained are given together with those obtained by alkaline purification only. We believe that both series of figures accurately express the relative yields of the three isomerides within the limits of error due to the method; as representations of the absolute yield, the results given by the silver salts are probably nearer the truth.

Dinitrohydroxy-1-o-*carboxyphenylmethylbenziminazole.*

From the trinitro-compound and anthranilic acid; crystallises from alcohol in two forms, ochreous scales and needles, both having the melting point 253°:

0·1772 gave 0·327 CO_2 and 0·0444 H_2O. C = 50·23; H = 2·78.
0·1787 ,, 23·5 c.c. N_2 (moist) at 13° and 765 mm. N = 15·64.
$C_{15}H_{10}O_7N_4$ requires C = 50·24; H = 2·81; N = 15·67 per cent.

The *silver* salt was prepared by adding a solution of silver nitrate to a solution of the ammonium salt of the iminazole from which excess of ammonia had been expelled by boiling. As there are two acidic hydrogen atoms in this compound, it was in the first place necessary to ascertain whether the salt contained one or two atoms of silver, and also how far the insolubility of the salt rendered it suitable for quantitative purposes:

1 gram iminazole gave 1·564 silver salt; the formula for a di-silver salt requires a yield of 1·597.

The salt is precipitated as a bright red powder, which, when dry, deflagrates strongly on heating, and is therefore somewhat difficult to analyse:

0·05 gave 4·15 c.c. N_2 (moist) at 15·5° and 765 mm. N = 9·76.
0·2344 ,, 0·0877 Ag = 37·42.
$C_{15}H_8O_7N_4Ag_2$ requires N = 9·81; Ag = 37·79 per cent.

The iminazoles of this series have all the properties of mixed phenols and carboxylic acids, and can be converted into esters by the usual methods.

Ethyl Ester.—Prepared by boiling the iminazole with absolute alcohol and a few drops of sulphuric acid for some hours in a reflux apparatus. Bright yellow needles from alcohol; m. p. 216°:

0·058 gave 7·1 c.c. N_2 (moist) at 15° and 770 mm. N = 14·53.
$C_{17}H_{14}O_7N_4$ requires N = 14·54 per cent.

Dinitrohydroxy-1-m-*carboxyphenylmethylbenziminazole.*

From the trinitro-compound and *m*-aminobenzoic acid; crystallises from glacial acetic acid as an ochreous, microcrystalline powder, or from alcohol, in which it is less soluble, in flat, ochreous needles; m. p. 273°:

0·1140 gave 0·2127 CO_2 and 0·030 H_2O. C = 50·88; H = 2·92.
0·1059 ,, 13·85 c.c. N_2 (moist) at 13° and 757·2 mm. N = 15·4.
$C_{15}H_{10}O_7N_4$ requires C = 50·24; H = 2·81; N = 15·67 per cent.

Silver Salt.—Prepared as above; a bright red powder:

0·371 iminazole gave 0·581 Ag salt. Calculated for di-silver salt, 0·592.
0·1550 Ag salt ,, 0·0581 Ag = 37·5. Di-silver salt requires Ag = 37·79 per cent.

Ethyl Ester.—Prepared as before; crystallises from alcohol in small, ochreous needles; m. p. 146°:

0·1024 gave 12·8 c.c. N_2 (moist) at 12° and 745·8 mm. N = 14·55.
$C_{17}H_{14}O_7N_4$ requires N = 14·54 per cent.

Dinitrohydroxy-1-p-*carboxyphenylmethylbenziminazole.*

From the trinitro-compound and *p*-aminobenzoic acid. Crystallises from glacial acetic acid in small, ochreous scales, or from alcohol, in which it is but sparingly soluble, as a pale, ochreous, microcrystalline powder. The compound chars and decomposes at 283—284°:

0·0814 gave 10·9 c.c. N_2 (moist) at 16° and 768·6 mm. N = 15·7.
$C_{15}H_{10}O_7N_4$ requires N = 15·67 per cent.

Silver Salt.—Prepared as before; bright red powder:

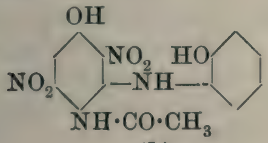
0·265 iminazole gave 0·403 silver salt. $C_{15}H_8O_7N_4Ag_2$ requires a yield of 0·422 gram.
0·1280 gave 0·0482 Ag = 37·66. The above formula requires Ag = 37·79 per cent.

Ethyl Ester.—Prepared as before. It appears that this modification requires a longer time for esterification than the isomerides, but this point requires further quantitative investigation. The ester dissolves with difficulty in alcohol, and crystallises in scales or needles of a pale ochreous colour. Both forms melt and decompose at 242°:

0·058 gave 7·1 c.c. N_2 (moist) at 13° and 766·5 mm. N = 14·59.
$C_{17}H_{14}O_7N_4$ requires N = 14·54 per cent.

The Aminophenol Series.

The methods of purification found most effective in this series have already been described. Owing to the circumstance that these iminazoles separate more slowly from the acidified alcoholic solution after dilution with water on completion of the reaction, it was found necessary to modify the quantitative method described in our last paper (*loc. cit.*, p. 1669) by adding a larger volume of hydrochloric acid (20 c.c. instead of 10 c.c. strong acid) and of water (400 c.c. instead of 200 c.c.). In other respects the process was unchanged. A point of special interest had to be considered in connexion with *o*-aminophenol. Supposing catenation to take place with this compound in the usual way, the product (I) might undergo further condensation in two ways.



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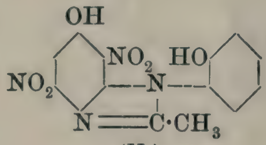

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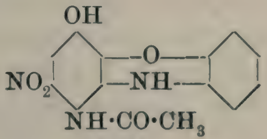
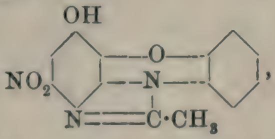


(III.)

If ordinary iminazole formation occurred, the product would have the above formula (II). It has been shown, however, by Turpin (Trans., 1891, 59, 722) that the product obtained from picryl chloride and *o*-aminophenol on heating with alkali loses nitrous acid and undergoes conversion into an oxazine. It was thus possible that instead of obtaining the expected iminazole we might have obtained the substituted oxazine (III), or a mixture of both compounds. A compound of mixed type,



is also conceivable. As will be seen from the results, it appears, however, that the iminazole condensation is predominant; no compound of the nature of an oxazine is formed.

Dinitrohydroxy-1-o-*hydroxyphenylmethylbenziminazole.*

From the trinitro-compound and *o*-aminophenol. The compound was purified by repeated crystallisation from dilute alcohol, with the addition of animal charcoal, and consisted of flat, pale ochreous needles, readily soluble in alcohol, and melting at 243—244°:

0·0904 gave 0·1685 CO_2 and 0·0267 H_2O. $C=50·83$; $H=3·27$.
0·0941 „ 0·1742 CO_2 „ 0·0279 H_2O. $C=50·51$; $H=3·29$.
0·0668 „ 9·7 c.c. N_2 (moist) at 16° and 762 mm. $N=16·97$.
$C_{14}H_{10}O_6N_4$ requires $C=50·87$; $H=3·11$; $N=17·0$ per cent.

Diacetyl Derivative.—As it had been previously observed that the iminazoles synthesised by means of the trinitro-compound readily acetylated on boiling with acetic anhydride, the ortho-nitro-group in the circumstances exerting but little protective action, it became of interest to study the products of acetylation in the present series, the members of which contain two (heteronucleal) hydroxyls. The product obtained by boiling the present iminazole with acetic anhydride for two hours, after crystallisation from alcohol with animal charcoal, consisted of pale ochreous needles, m. p. 165°. Analysis indicated that both hydroxyls had been acetylated:

0·0608 gave 7·15 c.c. N_2 (moist) at 9·5° and 745·3 mm. $N=13·48$.
$C_{18}H_{14}O_8N_4$ requires $N=13·55$ per cent.

Sulphonic Acid.—In the course of experiments having for their object the anhydridisation of the crude iminazole by heating with sulphuric acid, it was found that sulphonation took place quite readily both with this compound and its isomerides. The presence of hydroxyl in the *N*-phenyl group facilitates the entry of the sulphonic and nitro-groups, etc., to a remarkable degree when compared with the inertness of the unsubstituted iminazoles.

In order to prepare the sulphonic acid, the iminazole is dissolved in concentrated sulphuric acid and heated for an hour on the water-bath. On pouring into water, the sulphonic acid is slowly deposited in a crystalline form, and can be purified by dissolving in dilute alkali, filtering the solution, and precipitating by hydrochloric acid. The compound is thus obtained as scaly crystals of an ochreous colour, decomposing above 300°. When heated in a dry tube, it decomposes almost explosively:

0·1548 gave 16·8 c.c. N_2 (moist) at 10° and 761 mm. $N=13·01$.
0·3674 „ 0·2122 $BaSO_4$. $S=7·91$.
The monosulphonic acid, $C_{14}H_9O_6N_4{\cdot}HSO_3$, requires $N=13·66$; $S=7·81$ per cent.

The acid is not very soluble in cold water (0·018 gram in 170 c.c.), and, as the secondary products associated with the iminazole are converted by the action of concentrated sulphuric acid into compounds which are readily removed from the crystalline sulphonic acid by washing the latter with cold water, advantage was taken of this property to determine the yield of iminazole from the weight of sulphonic acid found. The numbers given in the previous part of this paper were obtained in this way after the alkaline treatment of the crude product to ensure anhydridisation, and after adding the correction necessitated by the loss due to the solubility of the sulphonic acid in water. The constitution of this acid has not been determined, although it is certain that the sulpho-group enters the *N*-hydroxyphenyl group, and most probably in the para-position with respect to the hydroxyl. It should be possible to synthesise the same sulphonic acid from the trinitro-compound and 2-amino-1-phenol-4-sulphonic acid. The secondary products removed by sulphonation amount to 27·2 per cent. of the crude iminazole.

Nitro-derivative.—Prepared by dissolving the iminazole in cold fuming nitric acid and pouring into water. After successive crystallisations from dilute alcohol and acetic acid, a yellow, micro-crystalline powder which darkens and decomposes at 265—270°. The compound is but sparingly soluble in alcohol or acetic acid :

0·1060 gave 16·6 c.c. N_2 (moist) at 16° and 765·3 mm. N = 18·4.
$C_{14}H_9O_8N_5$ requires N = 18·67 per cent.

The nitro-group is probably in the *N*-hydroxyphenyl group in the para-position with respect to the nitrogen atom, and it should therefore be possible to synthesise it from the trinitro-compound and 5-nitro-2-aminophenol.

Dinitrohydroxy-1-m-*hydroxyphenylmethylbenziminazole*

From the trinitro-compound and *m*-aminophenol. After crystallisation from alcohol with animal charcoal, the substance consists of ochreous scales, melting at 279° with previous darkening and partial decomposition. The crude product in this case, as in the case of all the meta-substituted amines, is highly coloured, the secondary product most probably consisting of an azo-compound :

0·1318 gave 0·2426 CO_2 and 0·04 H_2O. C = 50·58 ; H = 3·37.
0·069 ,, 9·9 c.c. N_2 (moist) at 15° and 764·4 mm. N = 16·9.
$C_{14}H_{10}O_6N_4$ requires C = 50·87 ; H = 3·11 ; N = 17·0 per cent.

The yield of iminazole in this case was determined by heating the crude product with concentrated sulphuric acid on the water-bath and pouring into water. The sulphonic acid remains in the solution, and the by-product separates out as a coloured resin, which can be collected, dried, and weighed. The loss as determined by this method is 3 per cent.

Diacetyl Derivative.—Prepared by boiling the iminazole for one hour with acetic anhydride; sparingly soluble in alcohol; small, pale orange needles, m. p. 209°:

0·07 gave 7·92 c.c. N_2 (moist) at 13° and 764 mm. N = 13·44.

$C_{18}H_{14}O_8N_4$ requires N = 13·55 per cent.

Nitro-derivative.—Prepared by dissolving the iminazole in cold fuming nitric acid and precipitation by water. After crystallisation from alcohol, ochreous scales; m. p. 260°, with slight decomposition:

0·0756 gave 12·2 c.c. N_2 at 16·5° and 764·7 mm. N = 18·88.

$C_{14}H_9O_8N_5$ requires N = 18·67 per cent.

Dinitrohydroxy-1-p-*aminophenylmethylbenziminazole.*

From the trinitro-compound and *p*-aminophenol. Purified by successive crystallisations from dilute alcohol and acetic acid. From the latter it separates in pale ochreous, lustrous scales, m. p. 245·5°, with previous darkening:

0·1075 gave 0·1998 CO_2 and 0·0321 H_2O. C = 50·7; H = 3·22.

0·0892 ,, 12·9 c.c. N_2 (moist) at 18·5° and 771·3 mm. N = 16·99.

$C_{14}H_{10}O_6N_4$ requires C = 50·87; H = 3·11; N = 17·0 per cent.

The yield of iminazole was determined in this case by sulphonation in precisely the same way as with the meta-isomeride, the by-product thus removed amounting to 5·8 per cent. of the crude product.

Diacetyl Derivative.—From the iminazole and acetic anhydride, as before. Pale ochreous needles from alcohol; m. p. 169·5°:

0·0656 gave 8 c.c. N_2 (moist) at 13·5° and 737·5 mm. N = 13·94.

$C_{18}H_{14}O_8N_4$ requires N = 13·55 per cent.

Nitro-derivative.—Prepared by dissolving the iminazole in cooled fuming nitric acid and pouring the solution into water. The compound separates from glacial acetic acid as a pale ochreous, microcrystalline powder, m. p. 252·5°:

0·0878 gave 13·7 c.c. N_2 (moist) at 13° and 765 mm. N = 18·56.

$C_{14}H_9O_8N_5$ requires N = 18·67 per cent.

The compound is therefore a mononitro-derivative, the nitro-group being most probably in the ortho-position with respect to the hydroxyl of the *N*-hydroxyphenyl group. The same compound would no doubt result from the interaction of the trinitro-compound and 2-nitro-4-aminophenol.

Of the other iminazoles synthesised in the course of this research for quantitative determinations of yield, those derived from α- and β-naphthylamine have already been described (Trans., 1906, **89**, 1942.) The mesidine compound is described below.

Dinitrohydroxy-1-(1 : 3 : 5-)*trimethylphenylmethylbenziminazole.*

From the trinitro-compound and mesidine in the usual way. The crude product required two alkaline extractions in order to remove the by-products. After successive crystallisations from dilute acetic acid and alcohol, the compound crystallised in small, ochreous scales, melting at 183° :

0·0606 gave 8 c.c. N_2 (moist) at 12° and 774·5 mm. N = 15·9.

$C_{17}H_{16}O_5N_4$ requires N = 15·77 per cent.

Dinitrohydroxy-1-p-*sulphophenylmethylbenziminazole.*

In order to ascertain whether the presence of a sulphonic group in the amine nucleus interfered with the formation of the iminazole ring, the interaction of the trinitro-compound and sulphanilic acid was investigated. In this case water was found to be the most appropriate solvent, the materials (1 mol. of trinitro-compound to 2 mols. of sulphanilic acid) being boiled in aqueous solution as long as nitrogen was evolved. If the solution is not too dilute, the iminazole crystallises out on cooling in yellow needles. Purification is best effected by dissolving the compound in dilute sodium hydroxide and precipitating by acid. This iminazolesulphonic acid dissolves in alkaline solutions with a deep orange colour; it is practically insoluble in alcohol, and has no definite melting point, but begins to decompose about 260° :

0·0772 gave 9·4 c.c. N_2 (moist) at 15·5° and 744·5 mm. N = 13·93.
0·1578 ,, 0·0962 $BaSO_4$. S = 8·29.

$C_{14}H_{10}O_8N_4S$ requires N = 14·21 ; S = 8·14 per cent.

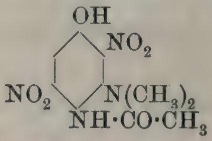
The main secondary product in this case is probably phenol-*p*-sulphonic acid, resulting from the decomposition by hot water of the diazosulphanilic acid formed by the action of the eliminated nitro-group on the free sulphanilic acid :

$$HO{\cdot}C_6H(NO_2)_3{\cdot}NH{\cdot}CO{\cdot}CH_3 + 2NH_2{\cdot}C_6H_4{\cdot}SO_3H = C_{14}H_{10}O_8N_4S + HO{\cdot}C_6H_4{\cdot}SO_3H + N_2 + 2H_2O.$$

Products from Secondary Amines.

The readiness with which the trinitro-compound reacts with dimethylamine is most remarkable in view of its inertness towards diethylamine. We have not yet ascertained whether methylethylamine gives a catenation product, but this amine will be investigated as soon as a supply can be obtained. The compound from dimethylamine is a derivative of dimethyl-*m*-aminophenol.

2 : 5-*Dinitro-4-acetylamino-3-dimethylaminophenol*,



The quantitative experiments with dimethylamine were carried out as follows: 2 grams of the trinitro-compound were dissolved in 30 c.c. of alcohol, and an excess (6 molecular proportions) of dimethylamine (33 per cent. solution in alcohol) added. The contents of the flask were kept boiling on a water-bath in the usual way, and, after completion of the reaction, diluted with 200 c.c. of water. Nothing separates at this stage, as the product, being phenolic, forms a soluble salt with the excess of dimethylamine. On adding 10 c.c. of concentrated hydrochloric acid, the product separates as an orange, crystalline deposit, which, after being kept for some hours, is collected, washed with cold water, dried, and weighed. The secondary product is no doubt dimethylnitrosoamine. The velocity of the reaction is such that the yield is not sensibly different in one and two hours respectively; smaller time intervals have not yet been allowed, but as the product is practically insoluble in cold water and very dilute alcohol, it may be possible to determine the rate of elimination of the nitro-group with considerable accuracy:

2 grams of trinitro-compound gave, in two hours, 1·57 of dimethylaminophenol derivative = 79·05 per cent. of theoretical yield.
2 grams of trinitro-compound gave, in two hours, 1·535 of dimethylaminophenol derivative = 77·4 per cent. of theoretical yield.
2 grams of trinitro-compound gave, in one hour, 1·6 of dimethylaminophenol derivative = 80·5 per cent. of theoretical yield.
2 grams of trinitro-compound gave, in one hour, 1·58 of dimethylaminophenol derivative = 79·9 per cent. of theoretical yield.

Mean of two-hour expts. = 78·23; of one-hour expts. = 80·2; mean of all experiments = 79·21.

It almost appears from these results as though the yield diminishes if the product is kept boiling in an alcoholic solution of the amine. It is not unlikely that slow decomposition may take place under these conditions, since we have found that the compound undergoes some more fundamental decomposition than simple hydrolysis when boiled with dilute alkali. This point will require further investigation, however, before any definite conclusion can be arrived at, since the difference in yield, which amounts to only about 2 per cent., may well be attributable to experimental error.

The pure compound dissolves but slowly in boiling alcohol, and separates, also very slowly, in dense, orange, rhombohedral crystals, melting and decomposing at 215° :

0·0958 gave 0·1483 CO_2 and 0·0406 H_2O. C = 42·21 ; H = 4·71.

0·2132 „ 35·3 c.c. N_2 (moist) at 9·5° and 756·9 mm. N = 19·78.

$C_{10}H_{12}O_6N_4$ requires C = 42·22 ; H = 4·25 ; N = 19·82 per cent.

The compound is strongly phenolic, dissolving in dilute aqueous alkali with an orange colour, and being precipitated as an ochreous powder on acidification. The *silver* salt was obtained by adding silver nitrate to a hot solution of the ammonium salt and allowing to cool, when silky, orange needles separated out :

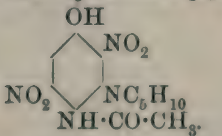
0·1888 gave, on ignition, 0·0512 Ag = 27·17.

$C_{10}H_{11}O_6N_4Ag$ requires Ag = 27·59 per cent.

The hydroxyl group in this compound is so well protected by the adjacent nitro-group that no methylation takes place on heating with silver oxide and methyl iodide in alcoholic solution. Acetylation also takes place to a very slight degree only on boiling with acetic anhydride, or on keeping for some days in acetic anhydride solution in presence of a little concentrated sulphuric acid. No definite acetyl derivative has been isolated from the crude product obtained by either of these methods. Attempts to hydrolyse the compound by acid and alkaline hydrolysing agents gave nothing definite ; the acetyl group does not appear to be removable without complete decomposition of the substance.

The dimethylamino-group in this compound is protected between ortho-substituents, and is therefore in a most unfavourable position for uniting with alkyl iodides. Attempts to form ammonium iodide derivatives by the direct addition of methyl iodide led to negative results under all conditions. The substance does not combine with methyl iodide when heated with an excess in a sealed tube at 100° in presence of a little magnesia. At a higher temperature (110—120°) methyl iodide causes complete decomposition, with the elimination of the dimethylamino-group. Experiments with dimethyl sulphate have so far also led to negative results, but this part of the work will be continued.

2 : 5-*Dinitro*-4-*acetylamino*-3-*piperidylphenol*,



The preparation of this compound was carried out as with the dimethylamine compound, piperidine being substituted for the latter base.

Two grams of trinitro-compound gave 1·655 grams of purified piperidyl compound after correction by alkaline treatment, and after adding the loss due to solubility (0·01 gram per litre). This yield corresponds with 73 per cent. of that theoretically obtainable.

The substance crystallises from alcohol in large, golden scales, m. p. 201°;

0·096 gave 14·1 c.c. N_2 (moist) at 16° and 768·6 mm. N = 17·32.

$C_{13}H_{16}O_6N_4$ requires N = 17·29 per cent.

Attempts to remove the acetyl group by acid or alkaline hydrolysing agents showed that some more fundamental decomposition than simple hydrolysis occurs, and no definite products have as yet been isolated. Experiments on the formation of ammonium derivatives from this compound are in progress.

The expenses of this research have been partly covered by a contribution from the Government Grant Fund of the Royal Society. We desire to express our indebtedness to this Fund and also to Mr. Harold E. Kuntzen, who has given us material assistance during the course of the work.

FINSBURY TECHNICAL COLLEGE.

CXVIII.—*The Preparation of Disulphides. Part V. Diethyl Esters of α-Dithiodibutyric, α-Dithiodi*iso*butyric, and α-Dithiodi*iso*valeric Acids.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

IT was shown in a former paper (Trans., 1908, **93**, 1645) that the esters of dithiodiglycollic and dithiodilactylic acids could be readily prepared by the electrolytic reduction of the mixture obtained from the interaction between sodium thiosulphate and the esters of halogen substituted acetic and propionic acids. This method of preparation has been extended to the esters derived from ethyl α-bromobutyrate, ethyl α-bromo*iso*butyrate, and ethyl α-bromo*iso*valerate. The esters so obtained are all liquids which are heavier than water, and distil without decomposition under diminished pressure. Diethyl α-dithiodibutyrate and diethyl α-dithiodi*iso*valerate possess the peculiar and not very disagreeable odour referred to in the previous communication as being characteristic of these dithio-esters, whereas diethyl α-dithiodi*iso*butyrate has an unpleasant, sickly odour. If, however, a trace of any of these esters, including those of dithiodiglycollic and dithiodilactylic acids, comes in contact with the benches of the laboratory, or the hands or clothing, decomposition takes place after a time, evidently with the formation of mercaptan compounds, since most disagreeable odours are produced, which are very difficult to dissipate. During the electrolytic reduction, some of these mercaptan esters are apparently formed at the same time as the dithio-compounds, since the same disagreeable odours are noticed. In spite of all precautions we were able to take, these odours gradually permeated the laboratory, and, in some one or two cases, the whole building, so that we have discontinued further work with these compounds for the present.

The preparation of the corresponding acids from the esters has only been completely successful in the case of α-dithiodi*iso*butyric acid, which is a solid melting at 197—198°. α-Dithiodibutyric and α-dithiodi*iso*valeric acids could not be obtained in the pure state,* since they apparently form syrupy liquids at the ordinary temperature. Professor Biilmann, of Copenhagen, informs us that he has also prepared α-dithiodibutyric acid by oxidation of α-thiolbutyric acid (*Annalen*, 1905, **339**, 351) with iodine, and its properties agree with those of the product obtained by us.

The melting points of the dithio-acids of this series, and, for the sake of comparison, those of the corresponding mercaptan acids and of the bromo-substituted fatty acids from which they are derived, are given in the following table:

Acid.	M. p.
Dithiodiglycollic	107—108°
α-Dithiodilactylic	142°
β-Dithiodilactylic	155
α-Dithiodibutyric	liquid
α-Dithiodi*iso*butyric	197—198
γ-Dithiodibutyric	108—109 *
α-Dithiodi*iso*valeric	liquid (?)

Acid.	M. p.
Thioglycollic	liquid
Thiolactylic	10·0°
Thiohydracrylic	16·8
α-Thiolbutyric	liquid
α-Thiol*iso*butyric	47·0°

Acid.	M. p.
Bromoacetic	50—51°
α-Bromopropionic	24·5°
β-Bromopropionic	62·5
α-Bromobutyric	liquid
α-Bromo*iso*butyric	48·0°
γ-Bromobutyric	32—33
α-Bromo*iso*valeric	44·0

* Gabriel, *Ber.*, 1890, **23**, 2490.

The great difference in the melting points of α-dithiodibutyric and α-dithiodi*iso*butyric acids is remarkable, but it corresponds with the difference in the melting points of the mercaptan acids from which they are derived, and also with the difference in the melting points of α-bromobutyric and α-bromo*iso*butyric acids. In fact, if the three series of acids are compared, it will be seen that the melting points, with the exception of that of bromoacetic acid, run parallel. α-Dithiodi*iso*valeric acid cannot be included in this comparison, since the purity of the product obtained (see later) was very doubtful. If the normal compounds in each series are compared, it will be noticed that substitution in the α-position with respect to the carboxyl group gives a compound of lower melting point than when the substitution takes place in the β- or γ-position; this is also true when the β-substituted derivative is compared with the γ-substituted derivative.

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* In attempting to prepare these acids from the esters, the odours met with are most disagreeable, and we have consequently not pursued the matter further.

EXPERIMENTAL.

Diethyl α-Dithiodibutyrate, $S_2(CHEt\cdot CO_2\cdot C_2H_5)_2$.—A mixture of 15 grams of ethyl α-bromobutyrate and 23 grams of sodium thiosulphate with 50 c.c. of water and 50 c.c. of alcohol (90 per cent.) was heated over a small flame under a reflux condenser for four hours. The reaction takes place very slowly (compare Slator and Twiss, Trans., 1909, **95**, 98), and even after prolonged heating there is a slight odour of unchanged ester. After cooling the clear solution so obtained, 75 c.c. of water were added (the addition of water caused the solution to become cloudy) together with 8 grams (theoretical quantity = 7·69 grams) of potassium hydrogen carbonate, and the resulting mixture was electrolysed in the cathode compartment of a divided cell, as described in the former paper (Trans., 1908, **93**, 1648). 0·25 Ampere was passed for about eight and a-half hours (theoretical current = 2·06 ampere-hours), 3 grams of potassium hydrogen carbonate being added after about three hours. During the electrolysis there was no unpleasant odour unless considerably more than the theoretical current was passed.

The ester, which separated as a heavy oil, was extracted with ether, and the ethereal solution well washed with water and dried. After evaporating off the ether, the remaining liquid was distilled under a pressure of 22 mm.; the main fraction, which formed the bulk of the distillate, passed over at 187°. The average yield of crude ester obtained in each experiment was 63 per cent.

Diethyl α-dithiodibutyrate is a colourless, fairly mobile liquid, heavier than water, with the peculiar and characteristic odour of these compounds:

0·2133 gave 0·3388 $BaSO_4$. $S = 21·81$.

$C_{12}H_{22}O_4S_2$ requires $S = 21·79$ per cent.

α-Dithiodibutyric Acid, $S_2(CHEt\cdot CO_2H)_2$.—In order to prepare this acid, some of the ester was heated with excess of aqueous hydrochloric acid for nine hours. The oil did not disappear, but a change had evidently taken place, since a yellow, viscous layer was formed in the place of the mobile ester. The hydrolysed product was extracted with ether, and the ethereal solution well shaken up with a slight excess of dilute aqueous potassium hydroxide in order to separate the acid from any unchanged ester. The alkali solution was then acidified with hydrochloric acid, and the α-dithiodibutyric acid extracted with ether. After drying and evaporating the ethereal solution, a yellow, viscous mass was obtained, possessing a faintly disagreeable odour. It was only sparingly soluble in water; the solution gave no coloration with ferric chloride, showing that no mercaptan acid was present, but it gave a precipitate with lead acetate, which was soluble in acetic acid. Reduction with zinc dust and acetic acid furnished the mercaptan acid (α-thiolbutyric acid), which gave a violet coloration with ferric chloride and decolorised iodine. The acid did not crystallise, even in a freezing mixture of ice and calcium chloride. After drying in a vacuum desiccator for some days, the equivalent was found to be 129 instead of 119, so that the substance evidently contained water or other impurity.

In a letter received from Professor Biilmann, he informs us that he has also obtained, by the oxidation of α-thiolbutyric acid with iodine, a viscous, yellow mass responding to the above tests, which he considers to be α-dithiodibutyric acid.

Attempts to prepare the acid by saponification of the ester with aqueous-alcoholic potash or baryta, either cold or hot, met with no success, since in each case decomposition took place (compare Trans., 1908, **93**, 1647) with the formation of a complex mixture containing mercaptan acids, and possessing a most disagreeable odour.

*Diethyl α-dithiodi*iso*butyrate*, $S_2(CMe_2 \cdot CO_2 \cdot C_2H_5)_2$, was prepared from ethyl α-bromo*iso*butyrate. The reaction mixture consisted of 15 grams of ethyl α-bromo*iso*butyrate, 27 grams of sodium thiosulphate, 80 c.c. of alcohol, and 80 c.c. of water, and was heated over a small flame for four hours, owing to the slow velocity of reaction. For the electrolysis 8 grams of potassium hydrogen carbonate were added, and the current passed for 2·75 ampere-hours (theoretical current = 2·06 ampere-hours), using 0·5 ampere for two and a-half hours and 0·25 ampere for the remainder of the time; about 3 grams of potassium hydrogen carbonate were added when the current was changed. During the electrolysis, the odours evolved were disagreeable in the extreme. The ester separated as a heavy oil; it was treated in the way already described, and finally distilled under diminished pressure. The first fraction, which passed over below 75°, evidently contained some mercaptan ester; the odour was unbearable, and permeated the building for some time. The average yield of crude ester was 30 per cent.

*Diethyl α-dithiodi*iso*butyrate* is a colourless, mobile liquid, heavier than water, and possessing a disagreeable, sickly odour. It distils at 165—166°/19 mm.:

0·1901 gave 0·3019 $BaSO_4$. S=21·81.

$C_{12}H_{22}O_4S_2$ requires S=21·79 per cent.

Lovén (*J. pr. Chem.*, 1886, [ii], **33**, 110) claims to have prepared this ester by shaking the ethereal solution of ethyl thiol*iso*butyrate with an aqueous solution of copper sulphate. He describes it as an oil with a most disagreeable odour; only a very small quantity was obtained, however, and it was neither purified nor analysed.

α-Dithiodi*iso*butyric acid, $S_2(CMe_2\cdot CO_2H)_2$, was prepared from the ester by saponification with alcoholic potash. After expelling the alcohol on the water-bath, the residue was dissolved in water, and the acid precipitated by the addition of hydrochloric acid. Some slight decomposition of the ester by the alcoholic potash occurred, and the crude acid had a somewhat unpleasant odour. On recrystallisation from water, however, in which it is only very sparingly soluble, it was obtained in colourless plates, which were inodorous, and melted at 197—198°.

The acid was also obtained by hydrolysis of the ester with aqueous hydrochloric acid, but the rate of hydrolysis was extremely slow.

This acid has also been prepared by Lovén (*J. pr. Chem.*, 1886, [ii], **33**, 110) and Biilmann (*Annalen*, 1906, **348**, 131), but neither of them give the melting point. At our request, Professor Biilmann has determined the melting point of his specimen, and finds it to be 196—197°, which agrees with our result:

0·1981 required 12·13 c.c. of 0·1366 $N/1$ NaOH for complete neutralisation. Equivalent=119·6.

$C_8H_{14}O_4S_2$ requires equivalent=119·1.

*Diethyl α-dithiodi*iso*valerate,* $S_2[CH(CHMe_2)\cdot CO_2\cdot C_2H_5]_2$, was prepared from ethyl α-bromo*iso*valerate, the method of procedure being similar to that for the other esters. The quantities of reagents taken were 12 grams of ethyl α-bromo*iso*valerate, 25 grams of sodium thiosulphate, 90 c.c. of water, and 90 c.c. of alcohol. The reaction with the thiosulphate took place very slowly, and even after boiling for nine hours some unchanged ester separated out on cooling. The clear solution was poured off from the unchanged ester and electrolysed in the usual way, after the addition of 7·5 grams of potassium hydrogen carbonate. The current was passed for about two and a-quarter ampere-hours (theoretical current = 1·54 ampere-hours), using 0·25 ampere. Potassium hydrogen carbonate, about 3 grams, was added during the electrolysis. After the reduction had been proceeding for some time, the odours became very disagreeable. The ester separated as an oil, but it was found best to allow the catholyte to remain overnight before it was extracted with ether and treated similarly to the other esters. The yield of crude ester was about 45 per cent., but it still contained some unchanged ethyl α-bromo*iso*valerate, since on distillation under diminished pressure the first portion of the distillate, which passed over below 100°, had a strong odour of that compound.

*Diethyl α-dithiodi*iso*valerate* distils at 173°/12 mm. It is a colourless liquid, and possesses only a very faint odour:

0·2059 gave 0·3009 $BaSO_4$. S = 20·07.

$C_{14}H_{26}O_4S_2$ requires S = 19·89 per cent.

*α-Dithiodi*iso*valeric acid*, $S_2[CH(CHMe_2)\cdot CO_2H]_2$, could not be prepared from the ester by saponification with alcoholic potash or baryta, owing to the decomposition which took place. The impure product prepared in this way had the most disagreeable odour we have experienced. Nor were we successful in obtaining a pure product by hydrolysis with hydrochloric or sulphuric acid. 2·6 Grams of the ester were treated in the same way as described for the preparation of α-dithiodibutyric acid, the heating with hydrochloric acid extending over twelve hours. Only 0·1 gram of acid was obtained, the greater part of the ester remaining unattacked. The acid formed a viscous mass, and did not solidify in a freezing mixture. It evidently contained some mercaptan acid, since the odour was disagreeable, and it gave a violet coloration with ferric chloride, and decolorised iodine to some extent. With lead acetate, it gave a white precipitate, as also with silver nitrate, the latter precipitate turning black on warming, especially in ammoniacal solution, owing to the formation of silver sulphide.

We have to acknowledge our indebtedness to the Committee of the Research Fund for a grant which partly covered the expense of the foregoing investigation.

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CXIX.—*The Chlorination of Acetanilide.*

By WILLIAM JACOB JONES and KENNEDY JOSEPH PREVITÉ ORTON.

THE original observations on the chlorination (and bromination) of acetanilide (Mills, *Proc. Roy. Soc.*, 1860, **10**, 589; *Annalen*, 1875, **176**, 352) apparently demonstrated that the para-derivative was the only monochloroacetanilide produced. Moreover, more recently Castoro (*Gazzetta*, 1898, **28**, [ii], 313), using a solution of chlorine in potassium hydroxide as chlorinating agent, recognised only *p*-chloroacetanilide. On the other hand, in the electrolytic reduction of nitrobenzene in the presence of hydrochloric acid, Löb (*Ber.*, 1896, **29**, 1895) obtained a mixture of *o*- and *p*-chloroanilines; he did not make an exact estimate of the proportion of each, but the former was obviously present in large proportion. In the action of acetylchloroamino-2:4-dichlorobenzene (Chattaway and Orton, Trans., 1901, **79**, 461) on aniline under certain conditions, the aniline was converted into a mixture of *o*- and *p*-chloroanilines in approximately equal proportions. Finally, the same authors (Trans., 1901, **79**, 469) recognised a small quantity of *o*-chloroacetanilide (5 to 8 per cent.) in the chlorination of acetanilide by bleaching powder in glacial acetic acid. In this case, the *o*-chloroacetanilide was isolated, not from the acetic acid mother liquor, but from the alcohol used to recrystallise the original solid product of the reaction.

As our attention had been repeatedly directed to the small yield (at most 40 per cent.) of pure recrystallised *p*-chloroacetanilide, a series of experiments has been carried out with the object of tracing the fate of the remainder of the acetanilide. As a result it has been found that in the chlorination of acetanilide by bleaching powder in acetic acid solution some 40 to 46 per cent. of the compound is converted into *o*-chloroacetanilide, which, owing to its high solubility, chiefly remains in the dilute acetic acid mother liquors.

Chlorination by chlorine in glacial acetic acid (at 15°) leads, however, to a different proportion of the two chloro-derivatives. The *o*-chloroacetanilide now represents about 30 per cent. of the acetanilide. To what cause this difference can be attributed, we are not at present able to decide. It is not due to the solvent, since the transformation of acetylchloroaminobenzene in glacial acetic acid solution yields *o*- and *p*-chloroacetanilides in the same proportion as the chlorination of acetanilide by bleaching powder.

Dilution of the acetic acid used as solvent does not affect the proportion of the acetanilides. When, however, the concentration of the acetic acid in the solvent falls to 2 per cent., 10 per cent. of the product consists of acetylchloroaminobenzene. On reducing the concentration of the acetic acid to 0·25 per cent., the yield of chloroamine rises to 64 per cent.; and if a large proportion of sodium acetate (20 grams per 100 c.c.) is present, the yield is further increased to 76 per cent.

This sensitiveness to the concentration of the acetic acid probably accounts for the divergent results of different observers in the repetition of Bender's (*Ber.*, 1886, **19**, 2272) original method of preparing acetylchloroaminobenzene by adding a dilute solution of bleaching powder to a suspension (or solution) of acetanilide in dilute acetic acid.

EXPERIMENTAL.

Chlorination of Acetanilide by Bleaching Powder Solution in Acetic Acid Solution.

A description of one of the experiments will illustrate the method finally adopted, after several trials, which has proved most effective in separating the products of the reaction.

One gram-molecular proportion of chlorine (497 c.c. of a 1·486*N*-solution of bleaching powder) was slowly run into a solution of 50 grams of acetanilide in 500 c.c. of glacial acetic acid. This operation occupied one hour, the mixture being kept at 8·5° and well stirred by a turbine. After twenty-four hours, the solid product was collected and dried. It weighed 32·9 grams, and consisted of *p*-chloroacetanilide mixed with 10 to 12 per cent. of the *o*-chloro-derivative. This proportion is estimated from the melting-point curve of mixtures of the two chloroanilides (see below).

The mother liquor from this first separation contains only a small quantity of the *p*-chloro-compound, together with the major proportion of the ortho-compound. Further dilution and prolonged keeping is followed by a partial separation of the para-derivative, mixed with still larger proportions (20 to 25 per cent.) of the ortho-compound. Since this second separation represented at most 8 per cent. of the acetanilide chlorinated, dilution of the mother liquor was not resorted to. Although the whole of the *o*-chloroacetanilide could be extracted from the mother liquor by chloroform, the following method of treatment was found to give the best results.

Hydrochloric acid was added to the mother liquor until the solution contained 10 per cent. of the acid, and the mixture was boiled for some hours. After rendering alkaline, the anilines were distilled in a current of steam. The liquid base thus obtained consisted mainly of *o*-chloroaniline mixed with a small proportion of *p*-chloroaniline and a still smaller proportion of 2:4-dichloroaniline. Their separation was achieved by distillation of their solution in sulphuric acid in a current of steam, a method first used by Beilstein and Kurbatoff (*Annalen*, 1875, **176**, 27).

The mixture of anilines extracted from the distillate by means of ether was dissolved in sulphuric acid, and the concentration of the acid adjusted to 3 per cent. This solution was now distilled in a current of steam, care being taken by appropriate heating of the distilling flask that the concentration of the sulphuric acid did not change by dilution or concentration. From this concentration of acid, the *o*-chloro- and the 2:4-dichloro-anilines rapidly distil, whilst the *p*-chloroaniline remains as sulphate, and can be distilled separately after rendering the liquid alkaline.

The *o*-chloro- and dichloro-anilines, which were extracted by ether from the distillate, were separated as follows: The mixture of anilines was dissolved in the least possible quantity of 3 to 5 per cent. sulphuric acid, the solution cooled to 0°, and the acid neutralised by titration with 10 per cent. sodium hydroxide. The dichloroaniline, which is the less basic as well as the less soluble (100 c.c. of water dissolve 0·07 gram at 11·9°), crystallises first, leaving the *o*-chloro-derivative dissolved in the faintly acid liquor. A little experience enables one to make a very sharp separation in this way. After rendering the solution alkaline, the *o*-chloroaniline was extracted with ether, and weighed as acetyl derivative, the melting point of which was 85° instead of 87°.

The results of such a quantitative estimation of the products of chlorination of acetanilide are given in the following table:

Acetanilide chlorinated	50·0 grams.
,, recovered as *p*-chloroacetanilide	25·4 ,,
,, ,, *o*-chloroacetanilide	22·0 ,,
,, ,, dichloroaniline	0·6 ,,
Loss	2·0 ,,

Proportion of Chloroacetanilides formed on Transformation of Acetylchloroaminobenzene.

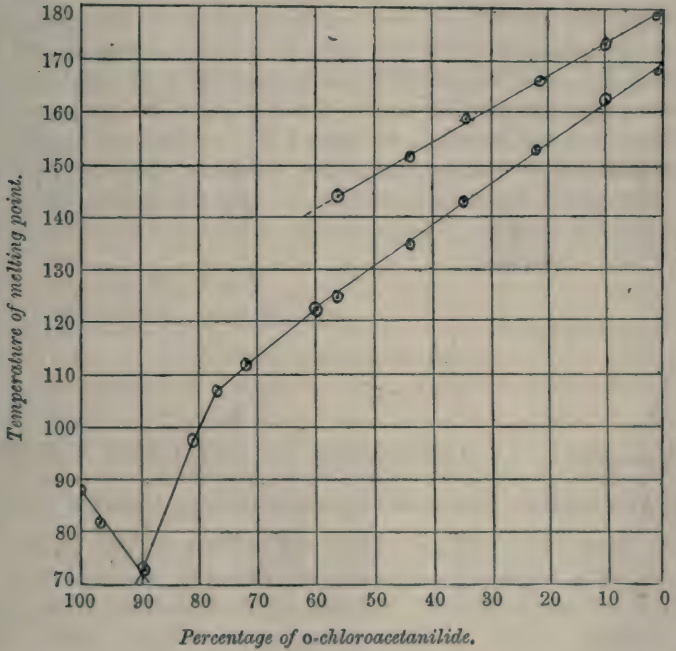
The chloroamine was dissolved in glacial acetic acid (10 per cent. solution), and one drop of concentrated hydrochloric acid added. The separation of the two chloroacetanilides was carried out as already described:

Acetylchloroaminobenzene used	9·6 grams	
p-Chloroacetanilide formed	4·92 ,,	= 9·34 grams,
o-Chloroacetanilide ,,	4·42 ,,	

Chlorination of Acetanilide by Chlorine.

When the chlorination was carried out in glacial acetic acid in the absence of sodium acetate, much dichloroacetanilide was formed, and hence some acetanilide remained unchlorinated. The hydrochloric acid combines with the acetanilide and shields it from attack. Chlorination in chloroform led to a similar result.

In the presence of one molecular proportion of sodium acetate, a trace only of dichloroacetanilide was formed. The separation of the products was carried out as described above.



Acetanilide chlorinated, 10 grams.	Expt. I.	Expt. II.
Acetanilide recovered as *p*-chloroacetanilide	6·67	6·64
,, ,, *o*-chloroacetanilide	3·01	2·80
,, ,, dichloroaniline	0·03	0·27
Loss	0·29	0·29

Melting-point Curves of Mixtures of o- *and* p-*Chloroacetanilides.*

The melting-point curves, which are shown in the figure on a small scale, bring out the fact that mixtures containing small proportions of the *o*-derivative have two melting points. Rapid cooling of a given molten mixture produces a solid, the melting point of which lies on the upper curve, and slow cooling that which lies on the lower curve. It is easy to tell by inspection of the solid on which curve the melting point will lie; the crystals of *p*-chloroacetanilide of higher melting point are elongated plates, whilst those of the lower are long, fine needles. The presence of anilides other than *o*-chloroacetanilide produces a similar phenomenon. It would appear, therefore, that *p*-chloroacetanilide is dimorphous, the melting point of one form being 179°, and that of the other, as estimated from the curve, about 169°. We have not been able to isolate the anilide of lower melting point in the pure state, but in the presence of 0·4 per cent. of *o*-chloroacetanilide we have obtained the two forms melting respectively at 178° and 168—169°. The very different melting points of the *p*-chloro-derivative given in the literature are probably accounted for by this peculiarity. As the proportion of *o*-chloroacetanilide increases above 50 per cent., the upper curve becomes impossible or very difficult to realise.

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CXX.—*Acids as Accelerators in Acetylation. Part II.*

By ALICE EMILY SMITH and KENNEDY JOSEPH PREVITÉ ORTON.

IN our first paper (Trans., 1908, **93**, 1242), it was shown that anilines of a non-basic character, for example, anilines with two negative ortho-substituents, reacted with acetic anhydride with a far greater speed in the presence of mineral acids. Thus acetylation could be quickly effected at the ordinary temperature even with diluted acetic anhydride. Moreover, it was found that the acetylation of phenols was greatly hastened by many acids and not only by sulphuric acid; in fact, perchloric acid showed itself superior to a "dehydrating" material such as sulphuric acid, whilst phosphoric oxide (and phosphoric acid) are incomparably inferior to either acid.

In order to follow quantitatively the effect of the nature and concentration of acids on the speed of acetylation by acetic anhydride, we have been obliged to confine ourselves, owing to experimental difficulties, to the acetylation of *s*-tribromophenol and the use of sulphuric, perchloric, and orthophosphoric acids.

The results demonstrate that the speed of acetylation is approximately proportional to the concentration of the acid. This relation is particularly well shown in the case of sulphuric acid, but is less well marked in the case of perchloric acid. For gram-molecular proportions, the rates of acetylation with these two acids are, at least when the concentration of the acid is small, in the ratio 2·5 : 1. Using orthophosphoric acid (or phosphoric oxide), acetylation was just perceptible under the same conditions of temperature and concentration after twenty-four hours, whilst in the presence of perchloric acid it was complete in 100 minutes. In the absence of any acid, no acetylation is detectable in six weeks.

It was suggested in a previous paper that the acetylation depends on the formation of a mixed anhydride of acetic acid and the mineral acid, for example, $CH_3{\cdot}CO{\cdot}O{\cdot}ClO_3$, a hypothesis which was supported by Franchimont, Skraup, and Thiele, and more recently by Stillich (*Ber.*, 1905, **39**, 1241), as accounting for the part played by sulphuric acid. An example of these mixed anhydrides has been obtained by Francis and Butler (*Ber.*, 1906, **39**, 3798, 3804), who isolated benzoyl nitrate, $C_6H_5{\cdot}CO{\cdot}O{\cdot}NO_2$, and showed that it gave with anilines a benzoyl derivative. Pictet and Khotinsky (*Compt. rend.*, 1907, **144**, 210) have prepared acetyl nitrate, the behaviour of which with anilines is quite similar. Since under the conditions of our experiments the phenol is attacked by nitric acid, a comparison of this acid as an accelerator with perchloric and phosphoric acids was impossible.*

Our results are in agreement with such a hypothesis. The speed of acetylation would be proportional to the concentration of this complex, which in its turn would be approximately proportional to the concentration of the acid, at least when the concentration

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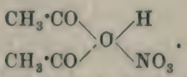
* In earlier papers (Trans., 1902, **81**, 806 ; 1908, **93**, 727 ; *Ber.*, 1907, **40**, 370) we have shown that a mixture of acetic anhydride and nitric acid diluted with acetic acid makes an excellent nitrating mixture for anilines, converting them into nitroamines, $Ar{\cdot}NH{\cdot}NO_2$, the acetyl derivative only appearing as a by-product, although the proportion becomes greater with unsubstituted anilines. We have suggested (Trans., 1908, **93**, 1242) that the acetyl nitrate reacts with the aniline mainly as follows :

$$CH_3{\cdot}CO{\cdot}O{\cdot}NO_2 + Ar{\cdot}NH_2 = Ar{\cdot}NH{\cdot}NO_2 + CH_3{\cdot}CO_2H,$$

whilst other acids yield mainly the acetyl derivative. In the light of the results of the authors cited above, it is obvious that acetyl nitrate, at least under certain conditions, yields only an acetyl derivative. Possibly the agent in nitration is a predecessor of the mixed anhydride, namely, an additive compound containing quadrivalent oxygen :



$$\begin{matrix} CH_3{\cdot}CO \\ CH_3{\cdot}CO \end{matrix} > O < \begin{matrix} H \\ NO_3 \end{matrix} .$$

In any case, we find that the formation of nitroamine is a far more rapid process than acetylation.

of the anhydride was very large relative to that of the acid. Further, inasmuch as the amount of this complex produced at a given concentration, and its reactivity with the phenol, would depend on the nature of the acid, the speed of acetylation would vary with the acid used. In the case of phosphoric acid, both factors may play a part in rendering it so inefficient.

The possibility of the agent being an additive complex of the acetic anhydride and the acid, in which the oxygen had become quadrivalent, that is, the compound which might be supposed to precede the acetyl perchlorate, etc., is, on the other hand, rendered more remote, as in that case no great difference would be expected between the various acids.

Solvents.—The effect of solvents other than acetic acid has also been investigated. In chloroform, benzene, or acetone, *s*-tribromophenol is not acetylated at the ordinary temperature. In the presence of sulphuric acid, acetylation is complete in chloroform solution in twenty minutes (concentration, temperature, and ratio of acetic anhydride to phenol were the same as were used throughout these experiments: see Experimental Part; ratio of sulphuric acid to phenol = 0·5 : 1 gram-mol.). Although a reaction took place in benzene and acetone solution, it was very much slower, sufficient acetate for a melting-point determination being formed only after sixty minutes.

Acetylation of Phenols.—As a practical method of acetylating phenols, from which acetyl derivatives are difficult to obtain, our experiments show that acids are far superior to sodium acetate as catalysts. A comparison of acids with pyridine, which was recommended by Verley and Bölsing (*Ber.*, 1901, **34**, 3354) as a catalyst in acetylation by means of acetic anhydride, has been made.

In acetic acid solution, pyridine was found to be nearly as effective as perchloric acid, and therefore considerably superior to sulphuric acid. When the pyridine and the phenol were in molecular proportions (the other conditions of concentration and temperature being identical with those which we have used throughout), only 10 per cent. of the phenol remained after thirty minutes. In chloroform solution, the reaction is more rapid, no phenol remaining after fifteen minutes. If pyridine is used as solvent, as in the usual method of acylation by acyl chlorides, the reaction is obviously still more speedy.

EXPERIMENTAL.

The measurements of the velocity of acetylation of *s*-tribromophenol by acetic anhydride in acetic acid solution in the presence of mineral acids were beset with many difficulties. In the first place, it was impossible to avoid an initial rise of temperature on mixing, owing mainly to the reaction of the acetic anhydride with the water unavoidably present either in the acetic acid or in the mineral acid. We find that acids very greatly quicken this interaction of acetic anhydride and water. This source of error could be, however, reduced to a minimum by mixing in a certain order.

The phenyl acetate produced in a given time and the unchanged phenol were directly weighed, the weights being corrected for the solubility of each in the media from which they had separated. This correction was determined by estimations of the solubility, and by carrying out separations of mixtures of known quantities of the phenol and the acetate.

The perchloric and phosphoric acids were used in the form of 50 per cent. aqueous solutions, and the sulphuric as the ordinary concentrated acid.

The following procedure was adopted after many trials as giving the most consistent results:

Two grams (1/16·5 gram-molecule) of *s*-tribromophenol (crystallised from light petroleum, and melting constantly at 95°) were dissolved in 30 c.c. of glacial acetic acid (m. p. 16·4°), and placed in the bath kept at 15°; 25 c.c. of redistilled acetic anhydride were mixed with 45 c.c. of acetic acid, and the mineral acid (measured in a standard burette graduated to 0·01 c.c.) added, whereupon a sharp rise of temperature took place. When the temperature of the latter mixture had fallen to 15°, the two solutions were mixed as rapidly as possible, the temperature rising 0·4—0·7°, but falling again to 15° within five minutes.

Ten c.c. of the mixture (that is, a volume containing 0·2 gram of the original phenol) were withdrawn at intervals, and added to 75 c.c. of warm (40—50°) water. After keeping for several hours, the suspension in dilute acetic acid was placed in a water-bath for two hours, filtered through a large Gooch crucible (which was fitted with filter paper), and washed with 50 c.c. of water at 15°. The crucible containing the solid was dried in an evacuated desiccator over sulphuric acid and phosphoric oxide. The phenol was then extracted from the solid by treatment with 25 c.c. of 2 per cent. sodium hydroxide for ten minutes at 15°, and the undissolved acetate collected in a Gooch crucible, washed in 50 c.c. of water at 15°, dried, and weighed. The phenol was isolated from the alkaline solution.

A series of experiments showed that the loss of phenyl acetate was 5 milligrams, which must therefore be added to the weight found in order to determine the amount of phenol acetylated. The loss of phenol was greater, amounting to 0·0134 gram.

The quantities of the mineral acids, sulphuric and perchloric, relative to one gram-molecule of *s*-tribromophenol, used in the various experiments were respectively 1/8, 1/4, 1/2, and 1 gram-molecule. With the higher proportions of perchloric acid, the concentration was halved in order to bring the reaction to a measurable velocity.

The following table summarises the results of one of the measurements, using perchloric acid, 1/8 gram-molecule:

Time (in minutes).	Acetate (corrected).	Phenol changed.	Percentage of phenol changed.	K_1.	K_2.
15	0·0373	0·0331	16·55	0·012	—
30	0·0643	0·0570	28·53	0·0112	—
45	0·0855	0·0754	37·72	0·0105	0·0092
60	0·1043	0·0925	46·27	0·0103	0·0095
90	0·1358	0·1205	60·25	0·0102	0·0098
120	0·1594	0·1415	70·74	0·0102	0·0099
135	0·1684	0·1494	74·74	0·0102	0·0099

K_1 is calculated from the equation:

$$dx/dt = k.c^{phenol} \times c^{acetic\ anhydride}.$$

The concentration of the acetic anhydride cannot be exactly determined, and since it is large relative to the phenol it may be taken as constant. Hence:

$$dx/dt = (k.c^{acetic\ anhydride}) \times c^{phenol} = K_1.c^{phenol}.$$

Under K_2 we have values of K_1 calculated after the reaction has proceeded for thirty minutes, when the effect of the initial rise of temperature is no longer felt.

The following values of K_1 and K_2 were found in a series of measurements when sulphuric acid is used as the accelerator:

Proportion of sulphuric acid to 1 gram-mol. of *s*-tribromophenol.	Mean values of K_1.	Mean values of K_2.
1/8 gram-mol.	0·0042	0·00372
1/4 ,,	0·0069	0·0064
1/2 ,,	0·0159	0·01334

The following values of K_1 and K_2 were found when perchloric acid was used as an accelerator:

Proportion of perchloric acid to 1 gram-mol. of *s*-tribromophenol.	Mean values of K_1.	Mean values of K_2.
1/8 gram-mol.	0·0107	0·0097
1/4 ,,	0·0178	0·0165
1/2 ,,	0·0378	0·0375
1 ,,	0·0556	0·0484

Our thanks are due to the British Association for a grant which has partly defrayed the cost of this investigation.

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CXXI.—*The Action of the Halogens on Aromatic Hydrazines.*

By Frederick Daniel Chattaway.

The actions which take place when the halogens are brought into contact with primary aromatic hydrazines are so violent, and so large an amount of tarry matter is generally formed, that they have been comparatively little investigated, and in consequence the formation of the many different substances which are produced when the conditions of interaction are altered has never been accounted for satisfactorily.

Emil Fischer, in the paper describing the behaviour of phenylhydrazine (*Annalen*, 1878, **190**, 67), states that he found the action of chlorine and bromine on it so difficult to follow by reason of the violent gas evolution that he mainly concerned himself with the action of iodine. As the chief end products of the latter action he obtained phenylazoimide and aniline. Fischer stated later in a footnote (*Annalen*, 1893, **272**, 214) that acetylphenylhydrazine can be directly brominated if dissolved in fuming hydrochloric acid, and Michaelis (*Ber.*, 1893, **26**, 2190) showed that acetyldibromophenylhydrazine ($N_2H_2Ac{:}Br{:}Br = 1 : 2 : 4$) and dibromobenzenediazonium chloride ($N_2Cl{:}Br{:}Br = 1 : 2 : 4$) were among the substances thus formed. Michaelis also found that under similar conditions phenylhydrazine itself could be brominated, *p*-bromophenylhydrazine hydrochloride and *p*-bromobenzenediazonium chloride being produced.

The action of substituted nitrogen chlorides on phenylhydrazine, which can be kept under control, was investigated some years ago by Chattaway and Orton (Trans., 1901, **79**, 467), and was shown to yield different products according as to whether the nitrogen chloride or the hydrazine was in excess. In the former case, chlorobenzene and nitrogen were the characteristic products, in the latter, phenylazoimide and aniline hydrochloride.

The author has recently shown (Trans., 1908, **93**, 852) that all primary aromatic hydrazines can be quantitatively converted into the corresponding diazonium salts either by chlorine or by bromine. If either halogen is allowed to act at a low temperature on the hydrazine dissolved in alcohol, the diazonium salt separates in a pure state. The conclusion was drawn that the formation of the solid diazonium salts is due to a substitution by halogen of two atoms of hydrogen in the $\cdot NH\cdot NH_2$ group, followed by the elimination of halogen hydride.

It was also shown (Proc., 1908, **24**, 172) that the replacement of hydrogen in the $\cdot NH\cdot NH_2$ group can be carried to completion, and that *N*-tribromo-substituted hydrazines, the so-called diazonium-perbromides, are produced quantitatively when the requisite amounts of bromine are added to aromatic hydrazines dissolved in acetic acid. As the first action of a halogen in replacing hydrogen liberates halogen hydride, in all the experiments hitherto made the interaction of halogen and hydrazine has taken place in presence of acids. From the behaviour of the primary aromatic hydrazines when oxidised, it seemed likely that evidence of the formation of the mono-*N*-halogen-substituted derivatives, which should be the first products of the interaction of primary aromatic hydrazines with halogens, would be obtained if the reactions were carried out in presence of alkalis. Such compounds, in presence of alkali, would be unstable, and might be expected to decompose into nitrogen, halogen hydride, and a hydrocarbon. A disubstituted *N*-chloro- or -bromo-hydrazine corresponding with the hydrogen chloride or hydrogen bromide additive product of a diazonium salt might be formed in small amount when the conditions were favourable, and would similarly decompose, yielding a mono-halogen-substituted hydrocarbon. These expectations have been completely realised. When chlorine or bromine is brought into contact with a primary aromatic hydrazine in presence of excess of potassium or sodium hydroxide, very vigorous action takes place, nitrogen is freely evolved, and the hydrazino-group, $\cdot NH\cdot NH_2$, is replaced by hydrogen; for example, benzene from phenylhydrazine, bromobenzene from *p*-bromophenylhydrazine, and toluene from *o*- or *p*-tolylhydrazine are produced.

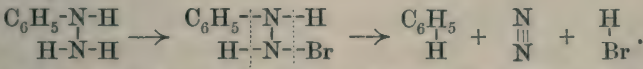
We thus have the interesting result that the action of halogen on an aromatic hydrazine in presence of alkalis causes the replacement of the hydrazino-group by hydrogen. At the same time, subsidiary reactions occur to a comparatively small extent, whereby simple azo-derivatives and hydrocarbons of the diphenyl series are produced, the former being obtained in relatively much larger amount than when the hydrazines are oxidised.

The author also finds that in acid solution the action of bromine on aromatic hydrazines, if sufficiently violent for the diazo-decomposition to take place, may give rise to more highly brominated hydrocarbons; for example, *p*-dibromobenzene, 1 : 2 : 4-tribromobenzene, and 1 : 2 : 4 : 6-tetrabromobenzene have been obtained from phenylhydrazine.

Any theory which attempts to explain the action of halogens on hydrazines must therefore account for the production of hydrocarbons, mono-, di-, tri-, and tetra-substituted hydrocarbons, azo-derivatives, azoimides, hydrocarbons of the diphenyl series, diazonium salts, unsubstituted and substituted in the aromatic nucleus, and diazonium perbromides.

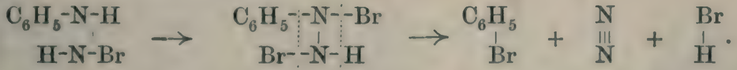
The complicated changes, which result in the formation of so many different compounds, all depend on a progressive substitution of hydrogen attached to the nitrogen, followed by a breaking down or intramolecular rearrangement of the *N*-substituted hydrazines thereby produced.

When a halogen acts on a primary aromatic hydrazine, one of the hydrogen atoms of the $\cdot NH\cdot NH_2$ group, probably one in the amino-group, is replaced,* a *N*-halogen derivative being formed. This, whilst comparatively stable in presence of acids, undergoes at once the typical diazo-decomposition in presence of alkalis, thus, for example:



$$\begin{array}{c}C_6H_5\text{-N-H}\\ |\\ \text{H-N-H}\end{array} \longrightarrow \begin{array}{c}C_6H_5\text{-}\vdots\text{-N-}\vdots\text{-H}\\ |\\ \text{H-}\vdots\text{-N-}\vdots\text{-Br}\end{array} \longrightarrow \begin{array}{c}C_6H_5\\ |\\ \text{H}\end{array} + \begin{array}{c}\text{N}\\ \equiv\\ \text{N}\end{array} + \begin{array}{c}\text{H}\\ |\\ \text{Br}\end{array}.$$

When a halogen, therefore, acts on a primary aromatic hydrazine in presence of an alkali, a hydrocarbon, the hydride of the aromatic group present in the hydrazine, is almost exclusively produced. When, however, an excess of halogen is employed, a relatively small amount of the *N*-monosubstituted hydrazine undergoes further substitution before disruption can take place, and a di-*N*-halogen substitution product is formed, which, like the mono-*N*-substituted hydrazine, although comparatively stable in presence of acids, undergoes the typical diazo-decomposition in presence of alkalis, a monosubstituted halogen derivative of the hydrocarbon formed in the first action being produced; for example,† phenylhydrazine yields bromobenzene, thus:



$$\begin{array}{c}C_6H_5\text{-N-H}\\ |\\ \text{H-N-Br}\end{array} \longrightarrow \begin{array}{c}C_6H_5\text{-}\vdots\text{-N-}\vdots\text{-Br}\\ |\\ \text{Br-}\vdots\text{-N-}\vdots\text{H}\end{array} \longrightarrow \begin{array}{c}C_6H_5\\ |\\ \text{Br}\end{array} + \begin{array}{c}\text{N}\\ \equiv\\ \text{N}\end{array} + \begin{array}{c}\text{Br}\\ |\\ \text{H}\end{array}.$$

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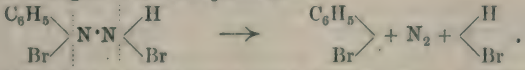
* This, as in similar cases, is probably effected by the addition of two atoms of the halogen to the nitrogen, followed by the elimination of a molecule of halogen hydride.

† It seems probable, owing to the more basic character of the amino-group, that addition of halogen and consequent replacement of hydrogen takes place first in this group. The further actions can be equally well explained whether the second replacement takes place in the $\cdot NHBr$ group or the $C_6H_5\cdot\underset{|}{N}H$ group; the second alternative is here employed, since the Blomstrand formula for diazonium salts is now generally adopted. The typical diazo-decomposition obviously can also be explained by assuming that it takes place thus:

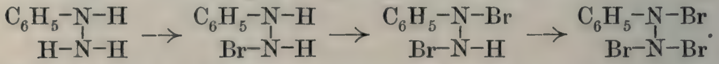


$$\begin{array}{c}C_6H_5\\ Br\end{array}\!\!>\!N\cdot N\!<\!\!\begin{array}{c}H\\ Br\end{array} \longrightarrow \begin{array}{c}C_6H_5\\ Br\end{array}\!\!> + N_2 + <\!\!\begin{array}{c}H\\ Br\end{array}.$$

The formulation adopted in the paper seems, however, more probable, recalling as it does the mode in which halogen hydride is eliminated from substituted hydrocarbons under the influence of alkali hydroxides.

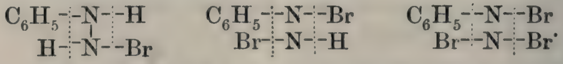
In presence of acids, the mono-*N*-substituted hydrazine being in these circumstances comparatively stable, the replacement of a second hydrogen atom by halogen takes place practically quantitatively, the whole of the hydrazine being thus converted into a di-*N*-halogen-substituted hydrazine. The affinity of the terminal nitrogen atom for the hydrogen and bromine atoms being now weakened by the more negative character of the $R-\underset{|}{N}-Br$ group, these are easily eliminated in presence of weakly basic substances, such as alcohol, and, therefore, if the action is carried out in alcoholic solution, a solid diazonium salt separates * (Chattaway, Trans., 1908, **93**, 852) on addition of ether.

The third and final stage in the replacement by halogen of the hydrogen attached to nitrogen in the aromatic hydrazines can be realised if bromine is employed, the *N*-tribromohydrazines—which are, in fact, the so-called diazonium perbromides—being produced. These, when heated, decompose into bromine, nitrogen, and a bromo-substituted hydrocarbon. Halogens, therefore, substitute the hydrogen attached to nitrogen in hydrazines atom by atom; for example, bromine acts on phenylhydrazine thus:



$$\begin{array}{c} C_6H_5-N-H \\ \vert \\ H-N-H \end{array} \longrightarrow \begin{array}{c} C_6H_5-N-H \\ \vert \\ Br-N-H \end{array} \longrightarrow \begin{array}{c} C_6H_5-N-Br \\ \vert \\ Br-N-H \end{array} \longrightarrow \begin{array}{c} C_6H_5-N-Br \\ \vert \\ Br-N-Br \end{array}.$$

Each of these *N*-halogen substitution products of the hydrazines can undergo the typical diazo-decomposition quantitatively. Thus, by the action of bromine on phenylhydrazine, either benzene or bromobenzene is obtained in this manner, nitrogen and hydrogen bromide or bromine being eliminated, thus:



$$\begin{array}{c} C_6H_5 \vdots -N- \vdots -H \\ \vert \\ H- \vdots N- \vdots -Br \end{array} \qquad \begin{array}{c} C_6H_5 \vdots -N- \vdots -Br \\ Br- \vdots -N- \vdots -H \end{array} \qquad \begin{array}{c} C_6H_5 \vdots -N- \vdots -Br \\ Br- \vdots -N- \vdots -Br \end{array}.$$

The formation of all the other products which, under varied conditions, have been obtained from the hydrazines by the action of halogens can be simply explained.

In presence of a considerable excess of hydrochloric or other strong acid, the basic $\cdot NH_2$ group is to a large extent protected against the action of the halogen,† and substitution takes place most readily in the $:NH$ group. The *N*-halogen compound thus produced is of the type of the acyl halogen amino-compounds, and under the influence of the acid undergoes the intramolecular rearrangement characteristic of these compounds, whereby the halogen passes into the para- or ortho-position in the nucleus; mono-, di-, and tri-substituted hydrazines are thus produced, whilst the higher substitution products of the hydrocarbons, for example, *p*-dibromobenzene, 1 : 2 : 4-tribromobenzene, and 1 : 2 : 4 : 6-tetrabromobenzene, are formed, when, owing to vigorous action, further substitution in the $\cdot NH\cdot NH_2$ group, followed by the typical diazo-decomposition, results, for example:

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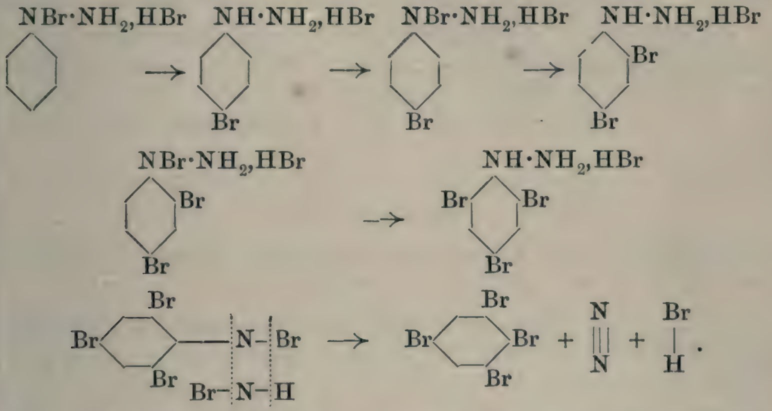
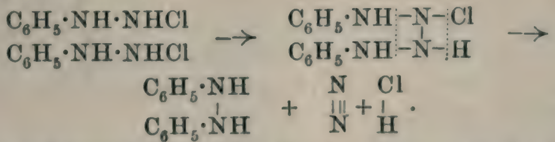
* As the interaction of halogen and hydrazine is usually very vigorous and accompanied by considerable evolution of heat, the diazonium salt may be decomposed, tarry matter being formed unless the action is carefully carried out with efficient cooling.

† This is probably owing to the union of the acid with the $\cdot NH_2$ group preventing the addition of halogen which is necessary before substitution can take place.



Even in presence of a large excess of acid, the $\cdot NH_2$ group is always to a considerable extent attacked, the yield of *p*-bromo- and 2 : 4-dibromo-substituted hydrazines therefore is never satisfactory, diazonium salts and their decomposition products always being produced in large amount.* The actual formation of 2 : 4 : 6-tribromophenylhydrazine or the corresponding diazonium bromide has not actually been observed, only 1 : 2 : 4 : 6-tetrabromobenzene, the product of its decomposition, having been isolated.

The various by-products produced in the subsidiary reactions, which take place when halogens react with hydrazines, can also be satisfactorily accounted for; for example, the production of azobenzene, in the formation of which two monosubstituted molecules take part, thus:



$$\begin{array}{l} C_6H_5\cdot NH\cdot NHCl \\ C_6H_5\cdot NH\cdot NHCl \end{array} \rightarrow \begin{array}{l} C_6H_5\cdot NH-N-Cl \\ \qquad\qquad\quad | \\ C_6H_5\cdot NH-N-H \end{array} \rightarrow \begin{array}{l} C_6H_5\cdot NH \\ \quad\;\; | \\ C_6H_5\cdot NH \end{array} + \begin{array}{c} N \\ ||| \\ N \end{array} + \begin{array}{c} Cl \\ | \\ H \end{array}.$$

The hydrazo-compound first formed is converted into diphenyl and into the azo-derivative by the further action of the halogen, followed by elimination of halogen hydride in presence of the alkali, thus:

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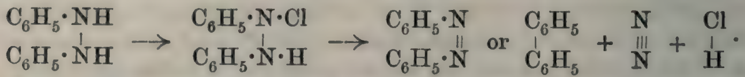
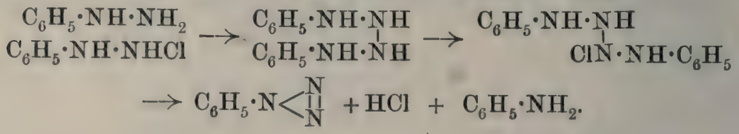
* Michaelis and Vaubel found that in the bromination of phenylhydrazine in presence of hydrochloric acid, less than half the hydrazine was converted into its substitution product.



$$\begin{matrix}C_6H_5\cdot NH\\ |\\ C_6H_5\cdot NH\end{matrix} \longrightarrow \begin{matrix}C_6H_5\cdot N\cdot Cl\\ |\\ C_6H_5\cdot N\cdot H\end{matrix} \longrightarrow \begin{matrix}C_6H_5\cdot N\\ \|\\ C_6H_5\cdot N\end{matrix} \text{ or } \begin{matrix}C_6H_5\\ |\\ C_6H_5\end{matrix} + \begin{matrix}N\\ |||\\ N\end{matrix} + \begin{matrix}Cl\\ |\\ H\end{matrix}.$$

Again, the monosubstituted molecule must react with the unsubstituted hydrazine to produce the azoimide and amine formed when the free hydrazine is present in excess; for example:



$$\begin{matrix}C_6H_5\cdot NH\cdot NH_2\\ C_6H_5\cdot NH\cdot NHCl\end{matrix} \longrightarrow \begin{matrix}C_6H_5\cdot NH\cdot NH\\ |\\ C_6H_5\cdot NH\cdot NH\end{matrix} \longrightarrow \begin{matrix}C_6H_5\cdot NH\cdot NH\\ |\\ ClN\cdot NH\cdot C_6H_5\end{matrix}$$

$$\longrightarrow C_6H_5\cdot N<\begin{matrix}N\\ \|\\ N\end{matrix} + HCl + C_6H_5\cdot NH_2.$$

EXPERIMENTAL.

Action of Potassium Hypochlorite on Phenylhydrazine in Presence of Potassium Hydroxide.

A $N/2$-solution of potassium hypochlorite was added in equivalent amount ($KOCl : C_6H_5\cdot NH\cdot NH_2$) to phenylhydrazine suspended in an excess of $4N$-potassium hydroxide; vigorous effervescence ensued due to escape of nitrogen, the liquid became warm, and a brownish-red, oily substance, having a strong odour of benzene, separated and floated to the surface. On passing steam through the fluid product, this red liquid distilled over and collected on the surface of the condensed water, a small quantity of red solid crystallising in the tube of the condenser towards the end of the operation. Only a small quantity of tarry matter was left behind in the alkaline residue. The red liquid was separated, dried, and fractionated; it proved to be a mixture of benzene and azobenzene, together with a very small quantity of diphenyl. The benzene obtained amounted to about 90 per cent. of the quantity theoretically obtainable from the phenylhydrazine used.

When a solution of potassium hypochlorite is added to an aqueous solution of phenylhydrazine, both being cooled to below 0°, the liquid becomes turbid, and a small quantity of a yellow solid separates. On adding a concentrated solution of potassium hydroxide, effervescence takes place, and benzene and azobenzene are produced as before.

The volume of nitrogen liberated in a number of experiments was measured; it corresponded within the limits of error with the amount of benzene produced. If, instead of adding the solution of potassium hypochlorite to the phenylhydrazine, the latter is added to the former, the action is in the main the same, but in addition to the benzene a little chlorobenzene is formed, and the amount of azobenzene produced is proportionally larger. In one experiment in which the quantities of each of these substances formed were determined, approximately ten parts of benzene to one part of chlorobenzene and two parts of azobenzene were obtained. The amount of tar produced is rather larger when this procedure is adopted. Similar experiments were made, in which the amount of alkali used was gradually diminished. These showed that diminishing the amount of alkali increased the yield of chlorobenzene and correspondingly diminished that of benzene.

When the hypochlorite is added to the phenylhydrazine without a large excess of alkali being present, in addition to benzene and azobenzene, phenylazoimide is formed.

Action of Acetylchloroamino-2:4-dichlorobenzene on Phenylhydrazine in Presence of Potassium Hydroxide.

Phenylhydrazine was mixed with about six times its weight of a 4*N*-solution of potassium hydroxide in alcohol, air being carefully excluded from the solution, which was cooled in a freezing mixture. To this was slowly added an equimolecular amount of acetylchloroamino-2 : 4-dichlorobenzene dissolved in about four times its weight of alcohol. Considerable heat was developed in the action, which was somewhat violent, much nitrogen was evolved, and a deep red-coloured liquid was produced. On distilling in a current of steam and diluting the distillate with water, a reddish-coloured, oily liquid separated. This was found to be composed approximately of 94 parts of benzene, 5 parts of chlorobenzene, and 1 part of azobenzene. A very little diphenyl was also present. Only a small quantity of tar was formed.

The actions of potassium hypochlorite and of acetyl chloroamino-2 : 4-dichlorobenzene in presence of alkalis on *p*-bromophenylhydrazine and on *o*- and *p*-tolylhydrazine were also investigated. The experiments made and the results obtained were precisely similar to those described above.

Action of Potassium Hypobromite on Phenylhydrazine in Presence of Potassium Hydroxide.

The experiment was carried out much as with potassium hypochlorite, except that an equimolecular quantity of potassium hypobromite was used. This was prepared by adding bromine to a strongly cooled *N*-solution of potassium hydroxide so long as its colour was discharged. The results were very similar to those obtained with hypochlorite; nitrogen was evolved, benzene, azobenzene, and a little diphenyl were formed. A rather larger amount of tarry matter was produced, and the yield of benzene was less than in the previously described experiment, about 70 per cent. of the benzene which theoretically might be obtained from the phenylhydrazine used was isolated.

If the mixture of aqueous potassium hydroxide and phenylhydrazine is added to the alkaline potassium hypobromite, a little bromobenzene is obtained in addition to the benzene and azobenzene, and the amount of this is increased if the quantity of alkali present during the action is diminished, or if a large excess of hypobromite is used. For example, in one experiment, in which the mixture of phenylhydrazine and potassium hydroxide was added to twice the equivalent quantity of potassium hypobromite, an amount of bromobenzene equal to one-sixth of the weight of the benzene formed was obtained. The action of a substituted nitrogen bromide, as, for example, acetylbromoamino-2 : 4-dichloroacetanilide or *N*-dibromobenzenesulphonamide, $C_6H_5 \cdot SO_2 \cdot NBr_2$, dissolved in alcohol on phenylhydrazine dissolved in alcoholic potash, also, is similar to that of the corresponding chlorine compound. Benzene is the main product, together with a little bromobenzene and azobenzene. *p*-Bromophenylhydrazine and *o*- and *p*-tolylhydrazines are acted on in a precisely similar manner by potassium hypobromite or substituted nitrogen bromides in presence of potassium hydroxide.

Action of Hypobromous Acid on Phenylhydrazine.

A *N*/3-aqueous solution of hypobromous acid, prepared by shaking yellow mercuric oxide suspended in water with bromine, was added to an equivalent quantity of phenylhydrazine. Nitrogen was evolved, and a brown, oily liquid separated. Steam was then blown rapidly through the liquid. At first, a pale yellow, oily liquid distilled over with the steam and condensed with the water, its density being slightly greater than that of water. When this oily liquid ceased to pass over, a small quantity of a colourless solid, which proved to be 2 : 4 : 6-tribromoaniline, crystallised out in the tube of the condenser. The yellow, oily liquid was found to be composed of approximately 15 per cent. of benzene, 40 per cent. of bromobenzene, 40 per cent. of phenylazoimide, and 5 per cent. of a solid residue, from which a little 2 : 4-dibromobenzene and 1 : 2 : 4-tribromobenzene, together with small quantities of *p*-bromoaniline and 2 : 4-dibromoaniline, were isolated.

Action of Bromine on Phenylhydrazine in Presence of Hydrochloric Acid.

The action of excess of bromine on phenylhydrazine dissolved in concentrated hydrochloric acid gives rise to *N*-tribromo-substituted phenylhydrazines, which, if the temperature is not kept low during the addition of the bromine, undergo the diazo-decomposition characteristic of these compounds, nitrogen being evolved, and bromo-substitution products of benzene being formed. The main product of such energetic bromination has been found to be always bromobenzene, but from among the products of such actions 2 : 4-dibromobenzene, 1 : 2 : 4-tribromobenzene, and 1 : 2 : 4 : 6-tetrabromobenzene have been isolated.

The thanks of the author are due to the Government Grant Committee of the Royal Society for a grant which has partly covered the expenses of this investigation, and to Professor Odling, who has placed a laboratory at his disposal.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CXXII.—*Some Physical Properties of Radium Emanation.*

By ROBERT WHYTLAW GRAY and SIR WILLIAM RAMSAY, K.C.B.

THAT radium emanation can be condensed by cold was discovered by Rutherford and Soddy in 1903 (*Phil. Mag.*, [vi], **5**, 561); Ramsay and Soddy, in the same year, proved that it obeyed Boyle's law; a preliminary measurement of the wave-lengths of its spectrum was carried out by Collie and Ramsay; Rutherford and Soddy, in 1902, and Ramsay and Soddy, in 1903, made experiments demonstrating the inactivity of the gas, which may therefore be taken as one of the argon series.

Two other radioactive elements also evolve inactive gases, namely, thorium and actinium. The emanation from thorium was shown by Rutherford and Soddy to resist the attack of the most powerful oxidising and reducing agents (*Phil. Mag.*, 1902, [vi], **4**, 581; 1903, [vi], **5**, 457); and it is practically certain that actinium emanation is also inactive. Attempts to determine the molecular weights of these gases by means of diffusion have yielded approximate results only in the case of radium emanation; the most trustworthy experiments appear to be those of Perkins (*Amer. J. Sci.*, 1908, [iv], **25**, 461), in which he compared the rates of diffusion of emanation and mercury vapour at 250° and 275°, and deduced the numbers 235 and 234 for the molecular and for the atomic weight of the emanation. On the other hand, P. Curie and Danne found 176; Bumstead and Wheeler, 180; and Makower, and Rutherford and Miss Brooks obtained similar results.

An excerpt from the periodic table shows the probable atomic weights of the higher members of the series, of which helium is the first member.

		N.		P.		As.		Sb.		?.		Bi.		?.
		14	(17)	31	(44)	75	(45)	120	(44)	164	(44)	208	(44)	252
		O.		S.		Se.		Te.		?.		?.		?.
		16	(16)	32	(47)	79	(48)	127	(42)	169	(43)	212	(45)	257
H.		F.		Cl.		Br.		I.		?.		?.		?.
1	(18)	19	(16·5)	35·5	(44·5)	80	(47)	127	(44)	171	(44)	215	(44)	259
He.		Ne.		A.		Kr.		Xe.		?.		?.		?.
4	(16)	20	(20)	40	(43)	83	(48)	131	(44)	175	(44)	219	(44)	263
Li.		Na.		K.		Rb.		Cs.		?.		?.		?.
7	(16)	23	(16)	39	(46)	85	(48)	133	(44)	177	(44)	221	(44)	265
Gl.		Mg.		Ca.		Sr.		Ba.		?.		Rd.		?.
9	(15)	24	(16)	40	(47)	87	(50)	137	(45)	182	(44)	226	(45)	271

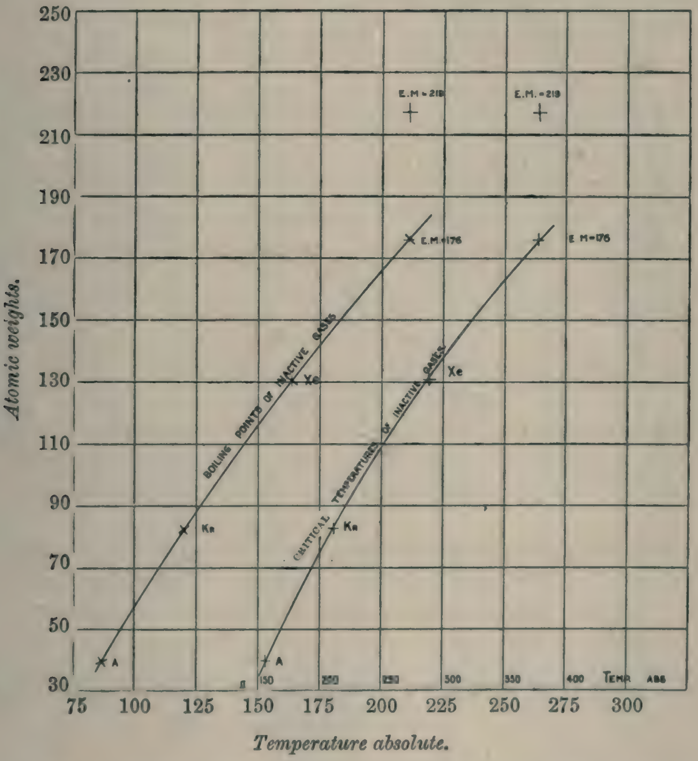
(The figures in brackets give the differences between consecutive atomic weights.)

It is obviously possible to decide which of the inactive gases occupies the position of the elements with atomic weights 175, 219, and 263, by determining their vapour-pressures. This has been now experimentally accomplished for radium emanation; the boiling point under atmospheric pressure is −62° or 211° absolute. The critical temperature has also been observed; it is 104·5°, or 377·5° abs. In Fig. 1 are shown the boiling points and critical points of argon, krypton, and xenon plotted against molecular weights. The lines lie on the arc of a circle; and this arc, if prolonged, cuts the ordinate on which the boiling point lies at the point representing the atomic weight 176. The critical point also lies on a similar arc, and gives the same value for the atomic weight of the emanation. If, on the other hand, the atomic weight be taken as 219, that of the second element after xenon, the boiling point would be 260° abs., 49 degrees higher; and the critical temperature, instead of 377·5°, would be 430° abs., no less than 53 degrees higher. Looking at the question from another point of view, the boiling and critical temperatures have been mapped on the assumption that the atomic weight is 219; it is evident that in no case could curves be drawn which with any probability would pass through these points.

Lastly, as seen in Fig. 2, the critical pressures of argon, krypton, and xenon also lie on the arc of a circle with much smaller radius than circles passing through the boiling and critical temperatures; this makes it more doubtful whether the position assigned to the emanation on the arc of this circle is justified; but, if it be placed on the circle, the atomic weight is again indicated as approximately

176. The volume of gas obtainable from unit volume of liquid has also been measured; but it is impossible to draw any useful deduction from this ratio; for, if the density of the gas be taken as 176/2, the liquid has a density which places it on a point on the almost straight line joining the densities of liquid argon, krypton, and xenon mapped against their atomic weights nearly on the 176 ordinate; if, however, the liquid be assumed to be derived from a gas of density 219/2, its density is proportionately higher, and it fits the curve at a point where the 219 ordinate intersects it.

FIG. 1.

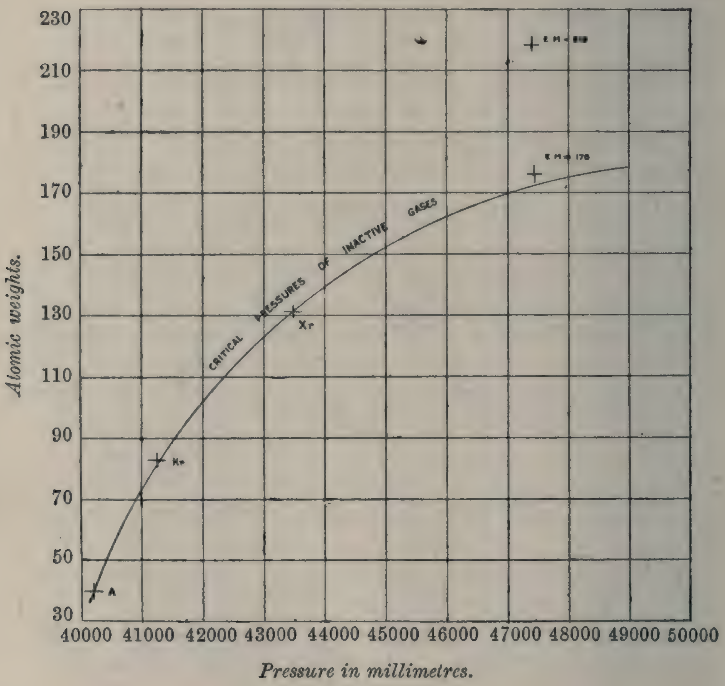


EXPERIMENTAL.

After a number of preliminary trials (of one of which an account has appeared: Proc., 1909, **25**, 82), three completely successful experiments were made, in which different quantities of emanation yielded by a solution of radium bromide containing 0·2111 gram of metallic radium were accurately measured, and then compressed in a modified Andrews' apparatus and their vapour pressures measured at different temperatures. The volume of the liquid was also determined.

(1) *Quantity of Radium Employed.*—The quantity of radium consisted of two lots of 50 milligrams each, bought from Buchner and Co., and tested not only against each other, but also against three different lots of bromide from the same source, all of which showed uniform γ-ray discharging power. This, of course, is no guarantee of purity; but, as Professor Giesel informed us that they were all extracted at different times, the fact of uniformity is in itself a strong presumption that the specimens were of high purity. This evidence, it may be remarked, is the same in nature as that of the purity of any chemical compound. The fact that a specimen of sodium chloride is considered to be pure depends on the quantitative agreement of one or more of its properties with those of other specimens prepared under different conditions. The remainder of the radium bromide was the sample kindly lent by the Vienna Academy (for data regarding its quantity, see *Sitzungsber. K. Akad. Wiss. Wien*, 1908, **117**, July). The total quantity of radium

FIG. 2.



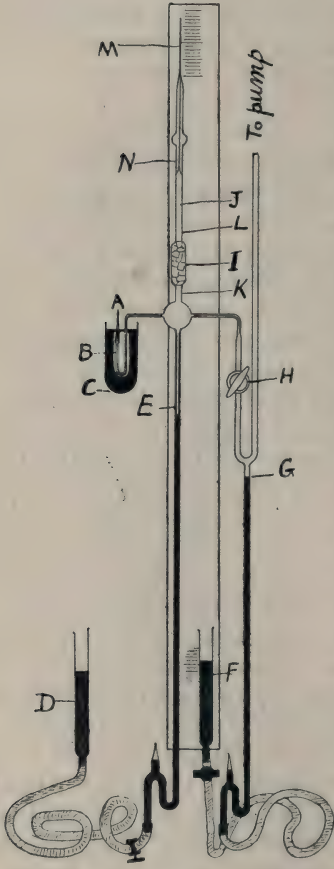
bromide used in these experiments was 0·3942 gram of $RdBr_2,2H_2O$, and the content of all in metallic radium (atomic weight = 226) was 0·2111 gram.

(2) *Method of Collection.*—The radium bromide contained in three bulbs in solution in water was in communication with a pump, by means of which the mixture of explosive gases could be withdrawn when required. After the curious change of rate of production of the explosive gases, described in a letter to *Nature* (December, 1908), of which a short account is given in the appendix to this paper, had ceased, the rate of evolution has remained quite constant at 25 c.c. every seven days, measured at atmospheric temperature and pressure.

This gas was stored for about an hour in the collecting-tube, the interior of which was coated with fused potassium hydroxide. It was then transferred in portions to an explosion burette, previously washed out with pure hydrogen, prepared from palladium-hydrogen; before each explosion, care was taken to draw the mercury past the stopcock, so that no contact was possible between the exploding gas and the grease of the tap. This residue always consisted of hydrogen, and varied in amount; we are unable to ascribe any cause to this variation. The residue, which was usually about 0·2 c.c. in volume, was transferred to a small tube, also previously washed out with hydrogen, the interior of which was coated with potassium hydroxide; the burette was washed out with about 1 c.c. of pure hydrogen into this tube, and the small amount of gas was left standing for an hour or more, to guard against the possible presence of carbon dioxide.

If the emanation comes into contact with grease, it apparently dissolves, and pure hydrogen is continuously generated; this renders it impossible to evacuate the apparatus perfectly; and it will be seen that the secret of success is due to the practical absence of "uncondensable" gas. To avoid contact with grease, the apparatus shown in Fig. 3 was employed. The cap *A*, ground to fit the constricted end of the inverted siphon *B*, was kept covered with mercury in the trough *C*; no grease was used, for the mercury itself made the joint a tight one. The reservoir *D* was lowered, so that the mercury stood at the level *E* in the vertical tube. Similarly, the reservoir *F* was lowered until the mercury stood at *G*, thus forming connection with the pump, when the tap *H* was opened. The tube *I* contained small lumps of quicklime freshly made from calc-spar. After evacuation, the apparatus was heated several times with a Bunsen flame until no further trace of gas could be extracted with the pump. In this way complete absence of absorbed gas on the interior walls of the tube was ensured, as well as on the lime in tube *I*. Hydrogen was then admitted through the inverted siphon *B*, by quickly removing the cap *A*, and at once depressing a small tube containing pure hydrogen over the inverted siphon. In a moment, the hydrogen enters, the tube is removed, and the cap replaced. This hydrogen was left in the apparatus overnight. Next morning, the apparatus was again pumped empty, and again heated until no trace of gas appeared in the fall-tube of the pump. Next, by raising the reservoir *F*, mercury passed the tap *H*, which was then closed. The emanation, mixed with hydrogen, was then admitted to the apparatus through the inverted siphon, and the cap replaced. The reservoir *D* was then raised until the mercury attained the level *K*; the gas was left in contact with the lime for about an hour; it is absolutely necessary that it should be dry, else moisture is continuously decomposed, and it is impossible afterwards to evacuate the apparatus. At this stage, the lime was heated. The tube *J* was then cooled with liquid air, contained in a moist paper cone, so as to condense the emanation; this was complete in twenty minutes. Both reservoirs were then lowered; the tap *H* was opened, and the hydrogen was pumped off until no trace of gas was visible in the capillary fall-tube of the pump. This fall-tube had a capacity of 2·3 cub. mm. per centimetre length, so that less than 0·0006 cub. mm. of gas could easily be detected at the top of the fall-tube. The mercury was then run up to *L*, and the liquid air in the paper cone, which needed constant renewal during these operations, was allowed to evaporate; the cone was then removed. After the emanation had volatilised, the mercury was run up, and the emanation was driven into the fine capillary tube *M*. Its volume was at once measured against the scale shown in the figure, at atmospheric, and also under diminished, pressure.

FIG. 3.



The tube was then cut at N, after raising the mercury in the reservoir to that level; and the tube was transferred to the compression apparatus, and compressed until liquid appeared. It was then jacketed at various temperatures, and the corresponding pressures were read.

(3) *Properties of the Liquid Emanation.*—The liquid emanation is colourless, and transparent, like water, when seen by transmitted light; it itself is, however, phosphorescent, and shines with a colour varying with the nature of the glass forming the tube in which it is confined; it might be more correct to say that it causes the glass to phosphoresce. The colour varies from blue to lilac; in silica, it is blue; in lead-potash glass, bluish-green; and in soda-glass, lilac; when compressed strongly in soda-glass, the colour reminds one of the cyanogen flame, at once blue and pink. On cooling further, the liquid solidifies, and ceases to transmit light; on warming, it again becomes transparent. This gave a means of determining its melting point, using a pentane thermometer, which registered correctly at the ordinary temperature and at the temperature of a pasty mixture of carbon dioxide and alcohol ($-78{\cdot}3°$: Travers, *Experimental Study of Gases*). The actual temperature at which the emanation mélts is $-71°$.

(4) *Properties of the Solid Emanation.*—On cooling further with alcohol cooled with liquid air, the colour of the phosphorescence changes. The solid glows with great brilliancy, like a small, steel-blue arc-light. Further reduction of temperature changes the colour to yellow, and in liquid air it is brilliant orange-red; the colour change takes place in inverse order on warming. The red phosphorescence disappears pretty sharply at $-118°$.

All these phenomena were observed with a microscope the objective of which was about one inch focal length.

(5) *Vapour Pressures of Radium Emanation.*—The tube containing the liquid was calibrated in the following manner: It was drawn from thermometer-tubing of regular bore; its diameter was about 1/20th mm. As it would have been impossible to weigh accurately the mercury, which formed a short thread in the tube, the somewhat varying capacity of the narrow capillary was found by comparing the length of a thread at a number of points by means of a travelling microscope. This thread was then sucked into the wider capillary of the thermometer-tube, and its length again determined. The volume of a known length of the thermometer-tube was determined by weighing the mercury which filled it.

The pressure was found to vary with the volume, even although liquid was present; this, as usual, was due to uncondensable gas.

To estimate its volume, pressure readings were taken with different quantities of liquid in the tube, at a series of constant temperatures; and, at the same time, measurements of the total volume of the gas and vapour were made. From these data, the pressure exerted by the uncondensable helium and hydrogen was calculated and subtracted in each case from the observed vapour pressure.

The ratio between the absolute temperature observed at any pressure and that of methyl alcohol at the same pressure was calculated for all the observations, varying between −10° and +104·5°, the latter being the critical temperature. These ratios were then mapped against the absolute temperatures of methyl alcohol, and gave a series of points through which a straight line could be drawn with small risk of error. From these observations, the vapour-pressure curve was calculated, and the divergence of each observation from the calculated temperature is given in the following table:

First Series.

Pressure in mm.	Ratio found.	Ratio smoothed.	Temperature found, ° abs.	Temperature smoothed, ° abs.
6224	1·478	1·492	273·0°	270·4°
6303	1·479	1·488	273·2	271·5
6553	1·474	1·486	275·5	273·2
9524	1·444	1·461	291·3	287·9
14055	1·439	1·439	303·0	303·0
14458	1·437	1·431	304·4	305·7
17345	1·416	1·418	314·9	314·5
17480	1·417	1·417	315·6	315·5
17779	1·414	1·415	316·1	316·3
17961	1·412	1·414	316·8	318·2
18713	1·409	1·411	318·7	318·4
18826	1·406	1·411	319·6	318·4
19997	1·402	1·403	322·5	322·3
21056	1·396	1·401	325·9	324·6
23572	1·383	1·392	332·9	330·7
24392	1·380	1·389	334·7	332·6
24865	1·379	1·387	336·0	334·0
26074	1·371	1·385	340·0	336·5
28295	1·365	1·375	344·0	341·9
28739	1·361	1·373	346·0	343·0
33618	1·355	1 359	354·0	352·8
36561	1·347	1·349	359·2	360·8
38065	1·340	1·347	362·6	362·9
38607	1·341	1·345	363·0	361·9
39215	1·339	1·341	364·2	363·8
41084	1·335	1·339	367·5	366·4
46051	1·330	1·325	374·0	375·4
47053	1·329	1·324	375·0	376·5

Second Series.

Pressure in mm.	Ratio found.	Ratio smoothed.	Temperature found, ° abs.	Temperature smoothed, ° abs.
5031	1·504	1·505	263·0°	262·9°
5528	1·495	1·496	266·8	266·7
6078	1·497	1·491	269·0	270·2
6654	1·499	1·486	271·0	273·3
11671	1·461	1·444	293·8	297·3
11703	1·462	1·444	293·7	297·3
14123	1·440	1·433	303·0	304·4
15132	1·437	1·422	308·0	311·2
17263	1·424	1·417	313·0	314·5
20024	1·399	1·405	323·0	322·4
22460	1·396	1·396	328·0	328·0
23709	1·384	1·391	333·0	331·3
27164	1·381	1·378	339·0	339·6
42026	1·303	1·336	377·5	368·3

In drawing the straight lines from which the smoothed ratios and smoothed temperatures are deduced, equal weight has been given to each observation; thus, in each series, if the algebraic sum of the minus and plus quantities be divided by the number of observations, it will be found that the quotients cancel out. Thus, although individual observations show considerable divergence from the smoothed values in many cases, the calculated temperatures may be taken as accurate. The vapour pressures of the emanation, calculated from the smoothed ratios, are given in the table which follows:

Vapour Pressures of Radium Emanation.

Pressure in mm.	Temp. ° abs.	Pressure in mm.	Temp. ° abs.	Pressure in mm.	Temp. ° abs.
500	202·6°	5000	262·8°	30000	346·0°
800	212·4	10000	290·3	35000	356·0
1000	217·2	15000	307·6	40000	364·4
2000	234·5	20000	321·7	45000	372·9
4000	255·3	25000	334·5	47450	377·5 (crit.)

Below 500 mm. pressure, the emanation is solid.

(6) *Volume of the Emanation.*—Three successful experiments were made; in the first of these, measurements made at atmospheric temperature and pressure gave for the emanation collected from 0·2111 gram of radium as bromide, during seven days, 0·0986 cub. mm., corrected to 0° and 760 mm. Measurements at 111·2 mm. and 16° gave 0·0882 cub. mm., corrected to 0° and 760 mm. The mean of these, 0·0934 cub. mm., was diminished by subtracting the volume of hydrogen and helium which it contained, namely, 0·0054 cub. mm.; the remainder is 0·0880. To that has to be added the volume of emanation pumped off, the quantity of

which was estimated by the relative γ-ray activity of the two quantities; this was 0·0032 cub. mm.; the total is 0·0912 cub. mm.

The second experiment gave at atmospheric temperature and pressure a volume 0·1060 cub. mm.; at 135·4 mm., the volume was 0·1106 cub. mm.; the mean is 0·1083 cub. mm. Subtracting the volume of the uncondensable gas, 0·0054, the remainder is 0·1029 cub. mm.; and adding the volume pumped off, 0·0037, the total volume is 0·1066 cub. mm. at 0° and 760 mm. This was obtained from the same quantity of radium in ten days.

In the third experiment, at atmospheric temperature and pressure, the corrected volume was 0·1271 cub. mm.; at 275 mm., the corrected volume was 0·1237 cub. mm., giving a mean volume of 0·1254 cub. mm., at 0° and 760 mm. The volume of impurity was 0·0083, and that of the emanation pumped off was 0·0064, making a final volume of 0·1235 cub. mm. This emanation had accumulated from the same quantity of radium in twenty-three days.

These results, calculated for the equilibrium quantity obtainable from 1 gram of radium metal, are as follows:

I. 0·604 cub. mm. at 0° and 760 mm.
II. 0·606 ,, ,, , ,,
III. 0·594 ,, ,, ,, ,,
Mean = 0·601 ,, ,, ,, ,,

This gives a half-life period for radium, on the two assumptions that the half-life period of the emanation is 3·86 days, and that the atom of radium, as well as that of the emanation is monatomic, of 1258 years.

Previous experiments by Cameron and Ramsay have shown larger volumes for the emanation; this is explainable by the fact that foreign gas remained mixed with the emanation; its presence has, as mentioned, been allowed for in the present research. The volume does not differ materially from the first observations of Ramsay and Soddy; but they, as well as Rutherford, neglected the original volume measured, in which foreign gas was undoubtedly present. It would appear that hydrogen and helium, in presence of the emanation, enter the walls of the tube; Mr. Usher, in this laboratory, has made quantitative observations on the point, which will be recorded later. The initial contraction of the gas, observed by Cameron and Ramsay, as well as by Ramsay and Soddy, and also by Rutherford, is undoubtedly due to this circumstance.

(7) *Volume of the Liquid Emanation.*—The gaseous emanation, confined in the narrow capillary tube connected with the pressure apparatus, was liquefied in each experiment, and the volume of the liquid was measured at atmospheric temperature; one

observation only was made at about the boiling point of the emanation; this is a difficult matter, owing to the freezing of the mercury at the low temperature. The length of column of the capillary tube occupied by liquid was measured with a reading microscope to the 500th of a millimetre, the volume of the conical end of the tube being estimated on the assumption that it was a perfect cone; little error is introduced by this assumption, as most of the liquid was in the cylindrical part of the tube. The results are stated in cubic millimetres of gas at 0° and 760 mm., yielded by 1 cubic millimetre of liquid:

(1) 461; (2) 686; (3) 535; (4) 623; (5) 447; (6) 581 (near boiling point of emanation).

The mean is 555. The actual volume measured was about 0·00025 cub. mm., and occupied about 0·24 mm. length of the tube. Of course, it varied in different experiments; these figures are given only to show the magnitude of the quantities measured.

The density of the liquid can be calculated only by assuming the density of the gas. If it be assumed that the atomic weight of the gas is 176, and the density 88, the density of the liquid becomes 4·6; the curve indicates that 4·8 would have been a more probable number. On the other hand, taking the atomic weight as 219, implying the density 109·5, the value would be 5·7; this number would equally well fit the curve. Until the actual density of the gas has been determined by weighing, it must be left doubtful which of these numbers is correct. But the strong presumption is in favour of the lower number.

We are well aware that the deduction drawn from these results, namely, that the emanation has the atomic weight 176, does not agree with the theory advanced by Rutherford regarding the progressive degradation of radium. Perhaps a non-radioactive substance is simultaneously produced when the emanation escapes from radium. It is possible to speculate that, instead of the equation:

$$\begin{array}{ccccccccccc} \mathrm{Ra} & = & \mathrm{He} & + & \mathrm{Em}, & \text{or} & \mathrm{Ra} & = & 2\mathrm{He} & + & \mathrm{Em} \\ 226 & & 4 & & 222 & & 226 & & 8 & & 218 \end{array}$$

the change actually occurring should be:

$$\begin{array}{ccccccccccccccc} \mathrm{Ra} & = & \mathrm{He} & + & \mathrm{X} & + & \mathrm{Em}, & \text{or} & \mathrm{Ra} & = & 2\mathrm{He} & + & \mathrm{X} & + & \mathrm{Em} \\ 226 & & 4 & & 46 & & 176 & & 226 & & 8 & & 42 & & 176 \end{array}$$

Appendix.

In November, 1907, the Imperial Academy of Science of Vienna was so kind as to lend one of us a relatively large quantity of what professed to be radium bromide of approximate purity. This sample, as well as two others, was dissolved in water in three bulbs, all of which were sealed to a Töpler pump, and use was made continuously of the emanation mixed with the decomposition products of water. The total amount of radium, as metal, was 0·2111 gram, and it produced about 25 c.c. of mixed oxygen and hydrogen every week. Much of the specimen from Vienna was insoluble in water; and it was found to consist largely of carbonate. On December 20th, 1907, some hydrobromic acid was introduced into the bulb containing the large quantity of radium; the insoluble matter all dissolved, with effervescence. For some months after this, bromine was evolved, and attacked the mercury of the pump; it ceased to appear in April, 1908. After that, the evolution of explosive gas was regular, until November, 1908. On November 11th, the normal amount of gas was produced; on that day, an apparatus, constructed of lead and paraffin, containing a mixture of mercuric chloride and ammonium oxalate, was placed by Dr. Flaschner close to the "Vienna bulb." On November 18th, there was "remarkably little gas; about 10 c.c." On November 25th, there were "only a few c.c." Suspecting a stoppage in the tap, air was introduced into the pump, the tap and tubes were cleaned, but there was no sign of a stoppage. The apparatus was again pumped to a vacuum, and left. On November 30th, only half a cubic centimetre was collected; on December 7th, about the same quantity; and on the 14th and the 18th, no greater amount was collected. On that date, Dr. Flaschner removed his apparatus, and after some hours replaced it, refilled. The emanation was not drawn, after this, until January 11th—three weeks later. Eight c.c. of explosive gas were collected. On that date, Dr. Flaschner finally removed his apparatus. On January 18th, 1909, 25 c.c. of gas, the old amount, were pumped off, and since then that volume has been collected weekly.

Experiments have, however, been made to try to reproduce the inhibiting conditions. First, the bulbs were surrounded by beakers containing the actinometric mixture employed by Dr. Flaschner; next, each bulb was placed in a lead cup, more than one-eighth inch thick; third, the lead cups were paraffined in their interior, and filled with the solution already referred to; and last, the identical apparatus used by Dr. Flaschner, charged as in his experiments, was placed as nearly as possible as he had placed it. But all to no purpose; 25 c.c. of explosive gas can be pumped off each week. We have failed to reproduce the conditions.

We are absolutely certain as regards the facts, and we are convinced that there has been no mistake. *Something* inhibited the action of the radium on water for a month and a half. Whatever that was, it was coincident in time with the presence of an apparatus placed outside the bulbs; when that apparatus was removed, the inhibition ceased. It may be remarked that the whole apparatus is in a locked room, and had not been disturbed.

UNIVERSITY COLLEGE,
LONDON.

CXXIII.—*Experiments on the Constitution of the Aloins. Part I.*

By ROBERT ROBINSON and JOHN LIONEL SIMONSEN.

DURING the course of a long series of researches on natural products which have been in progress in the laboratories of this University for some years, our attention was directed to the group of the aloins, and we decided with the concurrence of Dr. H. A. D. Jowett, who had already commenced to investigate this group, to endeavour to elucidate the constitution of the various members.

Tilden (Trans., 1877, **32**, 267) was the first to obtain a crystalline oxidation product from barbaloin, the principal member of this group. He treated an aqueous solution of barbaloin with potassium dichromate and sulphuric acid and obtained a substance, aloexanthin, to which he assigned the composition $C_{15}H_{10}O_6$. Oesterle and Babel (*Schweiz. Woch. Chem. Pharm.*, 1904, **42**, 329) have shown that Tilden's aloexanthin is a mixture of aloe-emodin and rhein, the latter being identical with rhein isolated from rhubarb by Hesse (*Annalen*, 1899, **309**, 43).

Hesse (*loc. cit.*), and also Oesterle (*Schweiz. Woch. Chem. Pharm*, 1903, **40**, 600), maintained that rhein has the composition $C_{15}H_{10}O_6$, and considered it to be a tetrahydroxymethylanthraquinone. Tschirch and Heuberger (*Arch. Pharm.*, 1902, **240**, 611), on the other hand, gave the substance the formula $C_{15}H_8O_6$, and the constitution of a methylene ether of a tetrahydroxyanthraquinone, basing this view on the facts that rhein on distillation with zinc dust gives anthracene, and on acetylation only yields a diacetyl derivative. More recently Oesterle and Tisza (*Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 701), having very carefully purified rhein, agree with this view, that it has the composition $C_{15}H_8O_6$, and our own analyses are in complete agreement with this result.

Since the yield of rhein obtained from barbaloin by any of the existing processes is extremely small, and the methods of isolation very laborious, we have in the first place endeavoured to improve them. After a long series of comparative experiments, we have succeeded in devising a simple method for obtaining more than fifty per cent. of the barbaloin employed in the form of rhein.

In attacking the problem of the constitution of barbaloin, we attempted in the first place to proceed on the lines which had been so successful in the case of brazilin and hæmatoxylin, namely, first to methylate the substance and then to investigate the degradation products formed on oxidation. This method proved, however, to be impossible, and we were unable to methylate barbaloin by any of the usual methods. We, however, soon discovered that valuable results could be obtained by the oxidation of the acetyl derivative of barbaloin with chromic acid in acetic acid and acetic anhydride solution.

In a preliminary note (Proc., 1909, **26**, 74), we have already briefly stated our views on the constitution of aloe-emodin and rhein. We consider that our experiments, taken in conjunction with the production of anthracene by zinc dust distillation, conclusively prove that rhein is a dihydroxyanthraquinonecarboxylic acid. We may perhaps briefly summarise our reasons for this opinion.

(*a*) Rhein yields only a diacetate, and this may be dissolved unchanged in a solution of sodium acetate. *Dimethylrhein*, prepared in the usual manner by the action of dimethyl sulphate and alkali on rhein, cannot be acetylated, and shows all the properties of a strong acid.

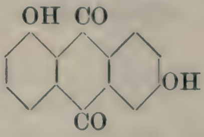
(*b*) The presence of a carboxyl group, indicated in (*a*), is also shown by the preparation of a *methyl* and *ethyl* ester in the usual manner, and these substances are readily hydrolysed to rhein. Rhein ethyl ester yields a *diacetate*, insoluble in alkalis, and, similarly, dimethylrhein yields an *ethyl* ester insoluble in alkalis.

(*c*) Still further evidence of the presence of the carboxyl group was obtained as follows: dimethylrhein yields the corresponding *acid chloride* when it is treated with thionyl chloride, and this is converted into dimethylrhein ethyl ester by boiling with alcohol.

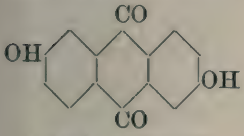
The acid chloride, $C_{14}H_5O_2(OMe_2)_2{\cdot}COCl$, gives with ammonia the corresponding amide, $C_{14}H_5O_2(OMe)_2{\cdot}CO{\cdot}NH_2$, which on treatment with alkaline hypobromite yields an *aminodimethoxyanthraquinone*.

Now, although the nature of rhein is thus clearly indicated, we have, as yet, not been able definitely to determine the position of the various groups.

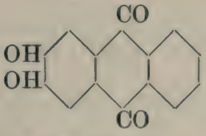
When the amino-group in aminodimethoxyanthraquinone is eliminated by diazotisation in the usual manner, a dimethoxyanthraquinone is obtained, and we propose now to give evidence which, in our opinion, indicates that this is the dimethyl derivative of *iso*chrysazin :



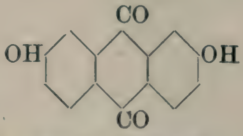
We are driven to this conclusion from the following facts. Rhein methyl ester, although it contains two hydroxy-groups, cannot be methylated by methyl iodide and alkali in alcoholic solution at 100° in a sealed tube. Consequently at least one of the hydroxy-groups must be in the ortho-position with respect to a carbonyl group of the anthraquinone nucleus, whilst the other must be similarly situated or be in the ortho-position with respect to the carboxyl group. This shows that rhein is not derived from anthraflavic acid, hystazarin, or *iso*anthraflavic acid.



Anthraflavic acid.



Hystazarin.



*iso*Anthraflavic acid.

On the other hand, the melting point of the dimethoxyanthraquinone (204—205°) is too high for the methyl ethers of quinizarin $[(OH)_2 = 1:4]$, purpuroxanthin $[(OH)_2 = 1:3]$, and *m*-dihydroxyanthraquinone $[(OH)_2 = 1:7]$, and too low for the methyl ethers of chrysazin $[(OH)_2 = 1:8]$ and anthrarufin $[(OH)_2 = 1:5]$. Furthermore, rhein cannot be alizarincarboxylic acid, because if this were the case one of the hydroxy-groups could not be methylated with dimethyl sulphate and an alkali. We have thus rejected nine of the ten possible dihydroxyanthraquinones, and are therefore forced to the conclusion that rhein is a derivative of the tenth isomeride, the little-known *iso*chrysazin or 1 : 6-dihydroxyanthraquinone. We are at present engaged in the further investigation of this part of the subject.

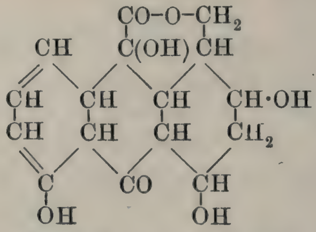
We may now consider the bearing of these observations on the question of the constitution of barbaloin. Oesterle (*Arch. Pharm.*, 1903, **241**, 604) has shown that aloe-emodin, one of the oxidation products of barbaloin, is oxidised by chromic acid to rhein, and since aloe-emodin is a trihydroxymethylanthraquinone and rhein is a dihydroxyanthraquinonecarboxylic acid, it is clear that one of the hydroxy-groups of aloe-emodin must be contained in a $CH_2\cdot OH$ group, and the oxidation may therefore be represented thus :

$$\underset{\text{Aloe-emodin.}}{C_{14}H_5O_2(OH)_2\cdot CH_2\cdot OH} + O_2 = \underset{\text{Rhein.}}{C_{14}H_5O_2(OH)_2\cdot CO_2H} + H_2O$$

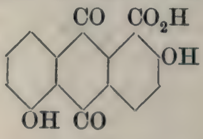
It is possible that the substance aloechrysin, $C_{15}H_8O_5$, which has been obtained by the oxidation of barbaloin (Oesterle, *Arch. Pharm.*, 1899, **237**, 81), may be the aldehyde intermediate between aloe-emodin and rhein.

These views have an important bearing on the constitution of barbaloin itself. According to the careful researches of Jowett and Potter (Trans., 1905, **87**, 878), barbaloin has the composition $C_{16}H_{18}O_7$ and contains four hydroxy-groups.

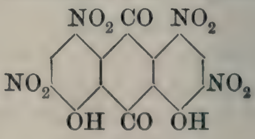
On treatment with nitric acid, it yields tetranitrochrysazin, whilst on oxidation with chromic acid an *iso*chrysazin derivative appears to be formed. This leads to the important conclusion that whilst one of the hydroxy-groups is contained in the unsaturated portion of a partly reduced anthraquinone, and one is situated in the same position as in anthranol, the two others are present in the completely reduced benzene nucleus. This leads to the following probable representation for barbaloin:



When barbaloin is subjected to the action of oxidising agents, a double change takes place, water is eliminated, in directions not yet definitely determined, from the alcoholic hydroxy-groups in the reduced benzene nucleus, and hydrogen and carbon dioxide are produced in the ordinary way. It will thus be readily understood that this expression for barbaloin can give rhein (I) on oxidation, and chrysammic acid



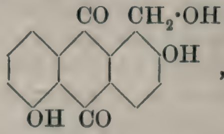
(I.)



(II.)

(II) by treatment with nitric acid.

The formation of the primary alcohol, aloe-emodin,



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by the action of alcoholic hydrochloric acid and oxidation would also be readily explained.

The further development of this subject depends on the exact determination of the constitution of rhein, and we are therefore extending our researches in this direction.

We wish to take this opportunity of expressing our indebtedness to Messrs. Burroughs, Wellcome & Co., and especially to Dr. Jowett, for the large quantity of pure barbaloin with which they have so kindly presented us.

EXPERIMENTAL.

Oxidation of Acetylbarbaloin.

Preliminary experiments indicated that a good yield of a crystalline oxidation product could be obtained when acetylbarbaloin * was oxidised by means of chromic acid in glacial acetic acid and acetic anhydride solution. As it was of great importance to obtain this substance in considerable quantities, a long series of comparative experiments were instituted, and ultimately the following process was found to give excellent results.

The acetylbarbaloin employed was prepared by boiling barbaloin (5 grams) with acetic anhydride (40 c.c.) and sodium acetate (5 grams) for three-quarters of an hour. After decomposing the acetic anhydride with water, the crude acetyl derivative was collected, and, after drying in the air, was, without further purification, used direct for the oxidation.

Acetylbarbaloin (5 grams) was dissolved in acetic anhydride (40 c.c.), and to the well-cooled solution a mixture of chromic acid (5 grams) dissolved in acetic acid (40 c.c.) and water (3 c.c.) was added in three portions. Much heat was generated, and the reaction was kept under control by cooling with water. After the addition of the chromic acid, the solution was kept for two hours with occasional shaking, the temperature being maintained at about 40—50°. Even before the reaction was complete the oxidation product began to separate as a yellow, crystalline powder on the sides of the flask. After two hours the solution was warmed on the water-bath until completely green, and then kept in the cold overnight. An equal volume of water was added, the yellow solid collected, washed with water, and dried at 100°. The yield was somewhat variable, the crude product weighing, as a rule, about 2·5 grams, this amount being, however, at times exceeded. The substance obtained in this way was found to consist of a mixture of acetylemodin and diacetylrhein, since, on hydrolysis, it yielded a mixture of rhein and emodin (see page 1091). When the crude product was repeatedly crystallised from glacial acetic acid containing acetic anhydride, it was obtained in beautiful pale yellow needles melting at 245°. Although this substance corresponds in all details with the diacetylrhein described by Hesse (*Annalen*, 1899, **309**, 43), by Tschirch and Heuberger (*Arch. Pharm.*, 1902, **240**, 611), and by Oesterle (*Schweiz. Woch. Chem. Pharm.*, 1903, **40**, 600), yet on analysis anomalous results were obtained. Of the following analyses, I and II were carried out with different specimens of the substance obtained directly from the oxidation, whilst III was a sample prepared from pure rhein and crystallised five times from acetic acid containing acetic anhydride:

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* We hope, in a future communication, to discuss the constitution of acetylbarbaloin.

I. 0·1694 gave 0·3752 CO_2 and 0·0545 H_2O. C = 60·4; H = 3·6.
II. 0·1324 „ 0·2932 CO_2 „ 0·0440 H_2O. C = 60·3; H = 3·7.
III. 0·1595 „ 0·3551 CO_2 „ 0·0476 H_2O. C = 60·7; H = 3·4.
$C_{19}H_{12}O_8,\frac{1}{2}H_2O$ requires C = 60.5; H = 3·4.
$C_{19}H_{12}O_8$ „ C = 61·9; H = 3·3 per cent.

The previous analyses of Hesse, Tschirch and Heuberger, and of Oesterle, agree quite well with the formula $C_{19}H_{12}O_8$, and further experiments are in progress with the view of purifying this substance. A rough determination of the acetyl groups was made by converting diacetylrhein into rhein ethyl ester by means of alcohol and sulphuric acid:

0·1988 gave 0·1693 rhein ethyl ester. $C_2H_4O_2$ = 14·9.
$C_{15}H_6O_4(OAc)_2$ requires $C_2H_4O_2$ = 16·9 per cent.

Diacetylrhein has already been described by the authors abovementioned, and the only additional properties of interest which we have observed have reference to its solubility in alkalis. Diacetylrhein is at once soluble in sodium carbonate or ammonia, yielding claret-red solutions, but it dissolves even in warm dilute sodium acetate, and is precipitated unchanged on the addition of a drop of acetic acid, this behaviour being strong evidence in favour of the presence of a carboxyl group.

Hydrolysis of the Oxidation Product.

The crude substance (20 grams) was suspended in methyl alcohol, and heated on the water-bath for fifteen minutes with a concentrated solution of potassium hydroxide (20 grams). Water was then added, and the deep claret-coloured solution acidified with hydrochloric acid, when a flocculent, yellow precipitate separated. The solution was boiled in order to render the precipitate crystalline, and the hot solution filtered and well washed with hot water. The mother liquors, on keeping, deposited a small quantity of an orange-coloured solid (see page 1091).

The product obtained in this way was a deep brown-coloured solid, and was purified by crystallisation from pyridine. Rhein was thus easily separated in a pure state in pale yellow needles melting at 310°:

0·1302 gave 0·3024 CO_2 and 0·0379 H_2O. C = 63·3; H = 3·2.
0·1326 „ 0·3079 CO_2 „ 0·0372 H_2O. C = 63·3; H = 3·2.
$C_{15}H_8O_6$ requires C = 63·4; H = 2·8 per cent.

Oesterle and Tisza (*loc. cit.*) have recently purified rhein by twenty crystallisations from pyridine and sublimation in the vacuum of a cathode ray light. The analysis then agrees with the formula $C_{15}H_8O_6$, the melting point being, however, raised to 321—321·5°, their previous value being 314°, which agrees well with that found by us.

Rhein is instantly soluble in sodium carbonate and ammonia. With ferric chloride it gives a brownish-red coloration. When heated in a sealed tube at 230° for four hours with glacial phosphoric acid, it may be recovered unchanged, and apparently shows no tendency to eliminate the carboxyl group. No benzoyl derivative insoluble in alkalis could be obtained from rhein by the Schotten-Baumann method.

The pyridine mother liquors from the purification of rhein deposited on standing an orange-coloured precipitate, whilst a further quantity of the same substance was separated from the mother liquors of the hydrolysis of the crude oxidation product (see page 1090). In order to obtain this substance in a pure state, it was dissolved in aqueous potassium hydroxide and shaken with benzoyl chloride, when a benzoate insoluble in alkalis was obtained. It was collected, dried, and recrystallised from benzene, when it separated in greenish-yellow needles melting at 234°. It therefore appeared probable that this substance consisted of tribenzoylaloe-emodin, which has the same melting point. The benzoate was hydrolysed with alcoholic potash, the diluted solution acidified with hydrochloric acid, and the brown precipitate collected, dried, and recrystallised from toluene, when it melted at 224°, which melting point was unaltered by admixture with aloe-emodin obtained by the action of alcoholic hydrochloric acid on barbaloin. Only a very small amount of aloe-emodin was obtained in proportion to the rhein.

Rhein Ethyl Ester, $C_{14}H_5O_2(OH)_2\cdot CO_2Et$.

This substance was very readily prepared from diacetylrhein by simultaneous hydrolysis and esterification.

Diacetylrhein (1 gram) was mixed with alcohol (30 c.c.) and sulphuric acid (3 c.c.), and boiled for an hour on the water-bath. The yellow acetate rapidly dissolved, and an orange-coloured solid gradually separated in beautiful needles. After cooling, the crystalline product was collected, and purified by recrystallisation from alcohol:

0·1586 gave 0·3800 CO_2 and 0·0544 H_2O. C = 65·3; H = 3·8.

$C_{17}H_{12}O_6$ requires C = 65·4; H = 3·5 per cent.

Rhein ethyl ester crystallises from alcohol in beautiful needles melting at 159°. It is only very sparingly soluble in alkali carbonates and ammonia. Its alcoholic solution gives with ferric chloride a deep red coloration.

Diacetylrhein Ethyl Ester, $C_{14}H_5O_2(OAc)_2\cdot CO_2Et$.—When rhein ethyl ester was acetylated in the usual manner with acetic anhydride and sodium acetate and the product poured into water, a yellow solid separated. This was collected, dried, and recrystallised from acetic acid:

0·1244 gave 0·2878 CO_2 and 0·0491 H_2O. C = 63·1; H = 4·4.

$C_{21}H_{16}O_8$ requires C = 63·6; H = 4·0 per cent.

Diacetylrhein ethyl ester separates from acetic acid in small, irregular plates, which melt at 170°. It gives no colour with ferric chloride, and is quite insoluble in cold aqueous potassium hydroxide.

Rhein Methyl Ester, $C_{14}H_5O_2(OH)_2\cdot CO_2Me$.

Rhein methyl ester is most conveniently prepared from diacetyl rhein by a similar process to that employed for the ethyl ester, but it has also been obtained by direct esterification of rhein. Rhein (5 grams) was boiled with methyl alcohol (100 c.c.) and sulphuric acid (5 c.c.) until complete solution had taken place. The orange solution was then allowed to cool, when beautiful deep orange needles crystallised out. These were collected and recrystallised from methyl alcohol:

0·1217 gave 0·2866 CO_2 and 0·0392 H_2O. C = 64·2; H = 3·6.

$C_{16}H_{10}O_6$ requires C = 64·4; H = 3·3 per cent.

Rhein methyl ester melts at 174°, whether prepared from rhein or diacetylrhein, and shows similar properties to the corresponding ethyl ester.

Methylation of Rhein.

I.—*Action of Sodium Methoxide and Methyl Iodide on Rhein Methyl Ester.*—In view of its importance on the constitution of rhein, an attempt was made to methylate rhein by the action of methyl iodide on the sodium compound of rhein methyl ester. Rhein methyl ester (1 gram) was dissolved in sodium methoxide (0·16 gram of sodium), when a claret-coloured sodium salt separated. After the addition of methyl iodide (1 gram), the mixture was heated in a sealed tube for ten hours at 100°. The solution, which had become almost colourless, was cooled, and the orange precipitate collected, washed with water, and dried, when it weighed 0·9 gram. On examination it was found to consist of unchanged rhein methyl ester, and no trace of a further methylated compound could be isolated, indicating that both the hydroxyl groups were adjacent to carbonyl groups.

II.—*Dimethylrhein*, $C_{14}H_5O_2(OMe)_2\cdot CO_2H$.

Pure rhein, dissolved in a solution of the calculated amount of aqueous potassium hydroxide, was shaken in the cold with a large excess of methyl sulphate, the solution being kept faintly alkaline by the addition of small quantities of potassium hydroxide from time to time. When all the methyl sulphate had been decomposed, the solution was rendered strongly alkaline with potassium hydroxide, causing the separation of the insoluble potassium salt of dimethylrhein. This was collected, the solution being filtered through cloth. The yellowish-brown salt was washed with concentrated potassium hydroxide solution and decomposed with dilute hydrochloric acid, when a flocculent precipitate was obtained, which became crystalline on boiling.

Dimethylrhein was purified by repeated crystallisations from alcohol, in which it is very sparingly soluble. After numerous crystallisations, it was obtained as light brown needles, which evidently contained solvent of crystallisation, since, on drying at 100°, they rapidly effloresced and became pale sulphur-yellow in colour. For analysis the substance was dried at 120—130° :

0·1124 gave 0·2695 CO_2 and 0·0430 H_2O. C = 65·4 ; H = 4·2.
0·1594 „ 0·2346 AgI. MeO = 19·4.
$C_{17}H_{12}O_6$ requires C = 65·4 ; H = 3·8 ; MeO = 19·9 per cent.

Dimethylrhein when quite pure melts at 283—284°. It dissolves in sodium carbonate and sodium acetate immediately and in the cold. The absence of phenolic hydroxyl is shown by the very faint colour with ferric chloride, and by the fact that its alkaline solutions have only a pale orange-yellow colour. Moreover, it can be neither acetylated nor benzoylated. When boiled with glacial phosphoric acid, the methyl groups are eliminated and rhein is obtained. It possesses a slightly bitter taste.

Dimethylrhein Ethyl Ester, $C_{14}H_5O_2(OMe)_2\cdot CO_2Et$.

Dimethylrhein (2 grams) was mixed with ethyl alcohol (60 c.c.) and sulphuric acid (6 c.c.) and heated on the steam-bath for twelve hours. This hot solution was filtered, and the yellow, crystalline residue washed with hot alcohol and finally crystallised from ethyl acetate :

0·1209 gave 0·2975 CO_2 and 0·0535 H_2O. C = 67·1 ; H = 4·9.
$C_{19}H_{16}O_6$ requires C = 67·1 ; H = 4·7 per cent.

Dimethylrhein ethyl ester separates from ethyl acetate in clusters of sulphur-yellow, feathery needles, melting at 185—187°. It is readily soluble in boiling acetic acid or ethyl acetate, but only very sparingly so in alcohol. It is quite insoluble in cold dilute potassium hydroxide, but on boiling with alcoholic potash it is hydrolysed and dimethylrhein is produced, as is shown by the analysis of a recrystallised specimen:

0·2237 gave 0·5375 CO_2 and 0·0829 H_2O. C = 65·5; H = 4·1.

$C_{17}H_{12}O_6$ requires C = 65·4; H = 3·8 per cent.

Dimethylrhein chloride, $C_{14}H_5O_2(OMe)_2 \cdot COCl$.

Dimethylrhein (1 gram) was gently boiled with thionyl chloride (15 c.c.) for a quarter of an hour. The rose-pink colour at first formed becomes yellowish-brown, and the substance passes into solution. The excess of reagent was then removed by evaporation over potassium hydroxide in a vacuum, when a bright yellow, crystalline mass was obtained, which was much darker in colour and not quite pure. The substance can be readily recrystallised by solution in chloroform and precipitation with light petroleum. In this way microscopic prisms are obtained melting at 190°, which are canary-yellow in colour, but darken somewhat on drying at 100°:

0·0930 gave 0·0400 AgCl. Cl = 10·5.

$C_{17}H_{11}O_4Cl$ requires Cl = 10·6 per cent.

Dimethylrhein chloride shows all the usual properties of an acid chloride of high molecular weight. It is not readily attacked by water, and may even be boiled with an aqueous solution of potassium hydroxide, in which it is quite insoluble, without decomposition. Prolonged boiling, however, results in its hydrolysis, and dimethylrhein is obtained on acidifying the solution. On boiling with alcohol, the substance quickly dissolves, and dimethylrhein ethyl ester separates from the cooled solution in clusters of needles, showing the correct melting point, which was unaltered by admixture with a sample of the ester prepared previously. The acid chloride gives a carmine-red colour in sulphuric acid solution.

Dimethylrheinamide, $C_{14}H_5O_2(OMe)_2 \cdot CO \cdot NH_2$.

Since the esters of dimethylrhein were found not to be readily attacked by ammonia, we prepared the amide by the action of ammonia on the chloride by the following simple method.

Dimethylrhein chloride (1 gram) was ground up into a fine paste with concentrated ammonia (15 c.c.) and allowed to remain in the cold overnight. The bright yellow colour of the chloride slowly changed to the pale yellowish brown of the amide, which was collected.

Dimethylrheinamide is very sparingly soluble in all organic solvents, and is most readily crystallised from a large quantity of ethyl acetate, from which it separates as a pale brownish-yellow powder, which was seen under the microscope to consist of beautiful hexagonal plates. The pure substance melts at 287°. For analysis it was dried at 100°:

0·1258 gave 4·9 c.c. N_2 at 8° and 752 mm. $N = 4·7$.

$C_{17}H_{13}O_5N$ requires $N = 4·5$ per cent.

Dimethylrheinamide dissolves with a carmine colour in concentrated sulphuric acid. It is only slowly hydrolysed by boiling with potassium hydroxide solution, more quickly with alcoholic potash, when dimethylrhein and ammonia are produced.

Aminodimethoxyanthraquinone, $C_{14}H_5O_2(OMe)_2 \cdot NH_2$.

This substance was prepared by the action of alkaline hypochlorite or hypobromite on dimethylrheinamide. The reaction was found to proceed more smoothly with the hypobromite.

The pure amide (2·5 grams) was treated with a solution of bromine (1 c.c.) dissolved in potassium hydroxide (3 grams) and water (40 c.c.). The reacting substances were intimately mixed in a mortar and kept for twelve hours. The bright yellow, gelatinous product was collected and washed with dilute aqueous potassium hydroxide. It was then dissolved in boiling water (150 c.c.), and the brownish-yellow solution acidified with hydrochloric acid. The red solution so obtained was filtered and rendered alkaline with potassium hydroxide. The brick-red precipitate of the base which separated was collected, washed with water, and purified by crystallisation from methyl alcohol, when it was obtained in magnificent ruby-red, rhombohedral prisms showing a green metallic reflex:

0·0962 gave 0·2378 CO_2 and 0·0405 H_2O. $C = 67·4$; $H = 4·7$.

$C_{16}H_{13}O_4N$ requires $C = 67·8$; $H = 4·6$ per cent.

Aminodimethoxyanthraquinone darkens very slightly at 230°, sinters at 240°, and melts at 243°. A specimen prepared in a similar manner with hypochlorite showed the same melting point, and was unaltered by admixture of the two substances. The base dissolves in concentrated sulphuric acid with a cherry-red colour, and in dilute hydrochloric acid, giving a yellowish-red solution. On the addition of sodium nitrite to the hydrochloric acid solution, the colour changes to pale yellow, owing to the diazotisation of the base. A deep purple colour is obtained in alkaline solution with β-naphthol, and on the addition of salt a purple dyestuff separates, which gives an intense blue colour in concentrated sulphuric acid. An almost black substance is obtained in alkaline solution with α-anhydrotrimethylbrazilone.

When the diazo-solution is boiled, the corresponding *phenol* separates as a yellow, crystalline precipitate, which crystallises from light petroleum in microscopic prisms melting at about 201°. It dissolves in sulphuric acid with a cherry-red colour, and in alkalis with a rose colour. It can be methylated, a fact which is of some importance and will be referred to in a future communication.

When the amine was dissolved in sulphuric acid and ethyl alcohol, an orange-red solution was obtained, which on the addition of amyl nitrite became yellow and a yellow precipitate formed. This consisted of the solid diazo-sulphate, and after solution in water shows the reaction of the diazo-salt. When the solid diazo-sulphate was boiled with alcohol, nitrogen was eliminated and the substance dissolved. On cooling, a yellow precipitate was obtained, which was repeatedly crystallised from acetic acid, when the pure substance melting at 204—205° was obtained. It crystallises in microscopic prisms, and is bright yellow in colour. It dissolves in sulphuric acid, giving a rather blue shade of crimson. It is quite insoluble in alkalis or acids, and there can be little doubt that it is a *dimethoxyanthraquinone.* The investigation of this substance is being continued.

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CXXIV.—*The Absorption Spectra of the Nitrates in Relation to the Ionic Theory.*

By EDWARD CHARLES CYRIL BALY, KATHARINE ALICE BURKE, and EFFIE GWENDOLINE MARSDEN.

PROFESSOR HARTLEY, in two important papers (Trans., 1902, **81**, 556, and 1903, **83**, 221), has described the absorption spectra of aqueous solutions of many nitrates, and has shown that these substances exhibit an absorption band in the ultra-violet. This absorption band is due to the NO_3-ion, for it is not obtained with the organic esters of nitric acid which are undissociated. Hartley draws the important conclusion from his results that, since the position of the absorption band of the metallic nitrates varies slightly with the position of the cation, there must be even in an entirely dissociated salt an intimate connexion between the ions. The two ions cannot be considered as independent entities for this reason, and in a previous paper (Baly and Desch, Trans., 1905, **87**,

766) this view has been emphasised and extended in dealing with the metallic derivatives of the aliphatic β-diketones. Hartley further pointed out that an alcoholic solution of lithium nitrate also exhibits the same absorption band as the aqueous solution.

In the present paper we describe the results of an investigation into the absorption spectra of solutions of the nitrates of lithium, ammonium, and silver, and of nitric acid in alcohol and in water, and in various mixtures of these substances.

The experiments were undertaken in the hope of throwing some light on the reaction velocities of silver nitrate and the alkyl iodides described by one of us with Professor Donnan (Burke and Donnan, Trans., 1904, **85**, 555). Although no fresh light was thrown in this direction, yet some interesting facts have been noted which bear on the ionic hypothesis and the theory of hydrated ions.

The solvents employed were as follows: Water, mixtures of water and alcohol, containing 75, 50, 40, 25, 10, 5, and 3 per cent. respectively of water, and, lastly, pure alcohol. The mixed solvents were made up by measuring definite amounts of water and making up to the necessary volume with alcohol. This method was adopted in order to obtain solvents with comparable numbers of water molecules. The strength of the solutions of the nitrates the spectra of which were examined was always decinormal, so that the absorption curves obtained are strictly comparable, the only variable being the water content of the solvent.

On comparing the absorption curves of the three metallic nitrates in the various solvents, a considerable variation in the persistence of the absorption band is to be observed, the persistence being defined as the change in dilution over which the band is visible. In order to compare the persistences of the absorption bands, it is only necessary to note the change in thickness of the solution over which the band is visible. Thus, in the case of a $N/10$-solution of ammonium nitrate in absolute alcohol, the absorption band was first visible through a thickness of 150 mm. of the solution, and it remained visible until the thickness was decreased to 30 mm. The persistence in this case may therefore be defined as equal to $150-30$, or 120 mm. In the case of the $N/10$-solution of ammonium nitrate in the solvent containing 3 per cent. of water, the absorption band only lasted over a range of $85-20$, or 65 mm. A very decided decrease in the persistence is thus observed when the solvent contains 3 per cent. of water.

In the following table, the persistences of the absorption bands are given for lithium, ammonium, and silver nitrates, and in Fig. 1 are given the curves obtained by plotting the persistence against the percentage of water in the solvent:

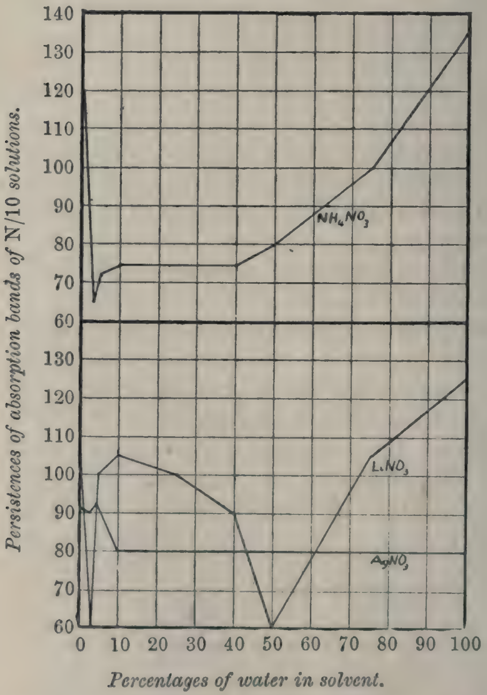
TABLE I.

Persistence of the Absorption Bands.

Percentage of water in solvent.	Lithium nitrate.	Ammonium nitrate.	Silver nitrate.
0	105	120	93
3	60	65	90
5	100	72	94
10	105	75	80
25	100	75	80
40	90	75	80
50	60	80	80
75	105	100	80
100	125	135	80

The three salts all show a minimum persistence at 3 per cent. of water, and lithium nitrate shows a second minimum at 50 per cent. of water. Silver nitrate differs from the other two, for, though there is a slight minimum at 3 per cent. of water, the persistence falls to a constant value at 10 per cent., and does not increase even with pure water.

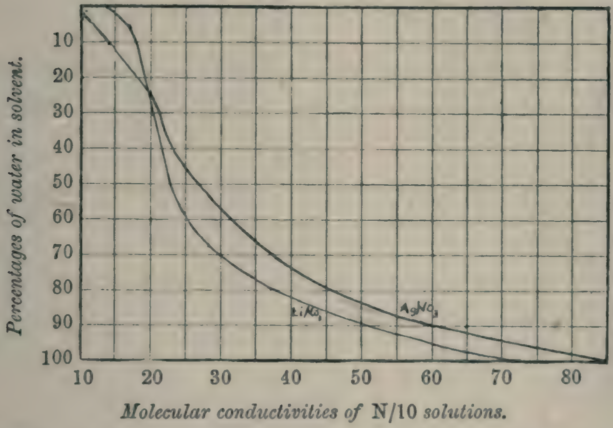
FIG. 1.



The first explanation which occurred to us was that the variations in the persistence were to be accounted for by changes in the ionisation of the salts. Evidently, if the absorption band be due to the NO_3-ion, as shown by Hartley, a decrease in the number of ions present will cause a decrease in the amount of the absorption exerted by the salt. In order to test this idea, we have measured the electrical conductivity of the $N/10$-solution of the three salts in the solvents mentioned above. We found, however, that in each case there is a steady rise in the conductivity as the water content of the solvent is increased. The curves obtained by plotting the molecular conductivities of lithium and ammonium nitrates against the percentage of water in the solvent are shown in Fig. 2.

It is evident from these curves that the variation in the persistence of the absorption bands cannot be due to variations in ionisation, for if there were a decided decrease in ionisation with 3 per cent. of water in the solvent, there must have been a corresponding decrease in the conductivity.

FIG. 2.



We next measured the molecular conductivities at infinite dilution, or, as usually called, the limiting conductivities. This was done in the ordinary way by diluting each solution with the appropriate solvent until the molecular conductivity became approximately constant, and then obtaining the true value by extrapolating the curve. These limiting conductivities, of course, only depend on the velocity with which the ions travel through the solution, and therefore any variation in the values must mean a variation in the velocity with which the ions move. These measurements were originally undertaken with the view of determining the amount of ionisation of the salts in $N/10$-solution, which, as is well known, is found by dividing the molecular conductivity at the $N/10$-concentration by the limiting conductivity.

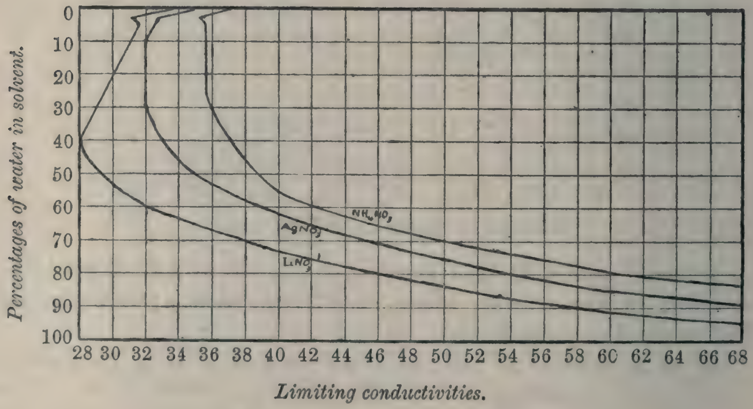
The complete series of values are given in table II, which shows the two molecular conductivities and the percentage of salt ionised at $N/10$-strength in each case (temperature = 15°):

TABLE II.

Percentage of water in the solvent.	Lithium nitrate.			Ammonium nitrate.			Silver nitrate.		
	Mol. cond. at $N/10$.	Limiting cond.	% of ion. at $N/10$.	Mol. cond. at $N/10$.	Limiting cond.	% of ion. at $N/10$.	Mol. cond. at $N/10$.	Limiting cond.	% of ion. at $N/10$
0	14·30	33·7	42·4	14·29	37·0	38·1	9·24	34·8	26·6
3	15·83	32·2	49·1	15·67	35·4	44·2	10·75	32·6	33·0
5	16·49	32·6	50·6	16·54	35·6	46·5	11·58	—	—
10	17·76	31·9	55·6	18·27	35·6	51·3	14·08	32·0	44·0
25	19·96	29·7	63·5	23·28	35·6	65·4	20·11	32·0	62·9
40	21·61	28·0	77·2	27·43	37·3	73·3	23·16	—	—
50	23·09	29·2	79·0	30·72	38·8	79·2	26·58	35·0	75·9
75	33·76	42·2	80·0	47·29	58·3	81·1	40·73	—	—
100	72·58	90·0	80·7	96·71	119·0	81·3	85·44	103·0	82·9

In Fig. 3 are shown the curves of limiting conductivity plotted against percentage of water in the solvent, and the most striking fact to be noticed is that the limiting conductivities show similar variations to the persistences of the absorption band (see Fig. 1), a resemblance which is all the more noteworthy when the values of the ionisation at $N/10$-strength are taken into account. For example, on the addition of 3 per cent. of water to the solvent, the ionisation of a $N/10$-solution of ammonium nitrate in absolute alcohol *increases* from 38·1 to 44·2 per cent., whilst the limiting conductivity *decreases* from 37·0 to 35·4, and the persistence of the absorption band *decreases* from 120 to 65. Thus, although the ionisation increases, the amount of absorption is very materially

FIG. 3.



decreased. The explanation of this anomaly must be sought for in the decrease of the limiting conductivity, for the agency which causes a decrease in absorption also causes the ions to move more slowly through the solution. There seems little doubt that hydration of the salt by the water must take place, for it is evident that the velocity with which the ion travels must be decreased if it be loaded with a mass of water-molecules. There is every reason to believe that the hydration of a molecule or ion of a dissolved salt depends on its residual affinity and that of the solvent molecules. The NO_3-group naturally possesses considerable residual affinity, and the absorption band must be due to the play of forces amongst this residual affinity. When the NO_3-group is hydrated, a portion of the residual affinity will be satisfied by virtue of the combination with the water-molecules; there will thus be left less free affinity, and the absorption exercised will be diminished. The decrease in both absorption and the velocity of migration of the ions can thus be explained by hydration.

If the hydration of the salt reaches a maximum with 3 per cent. of water in the solvent, the addition of a greater amount of water to the solvent will serve to provide a mechanism by means of which the hydrated ions can be handed on through the solution. An increase in the quantity of water beyond that required for the hydrating process must therefore increase the values of the limiting conductivities, and unless further hydration takes place the limiting values will tend to increase from those at 3 per cent. to those at 100 per cent. of water. This is true for ammonium nitrate, for the curve (Fig. 3) shows a general tendency to rise after the 3 per cent. of water point, although the rise at first is very slow; moreover, the curve has generally the same shape as the persistence curve in Fig. 1. The case is very similar with silver nitrate, for although the minimum due to hydration is not reached until the solvent contains 10 per cent. of water, yet the curve resembles that of ammonium nitrate.

Lithium nitrate differs from the other two salts, for from the curves of both persistence of absorption band and limiting conductivity there is strong evidence that a further hydration takes place up to about the point 45 per cent. of water. It would seem that there can be no other explanation than that the lithium and NO_3-ions can exist in two states of hydration, the first when the solvent contains 3 per cent. of water, and the second when there is about 45 per cent. of water in the solvent. The strongest argument for hydration lies, of course, in the decrease of the persistence of the absorption band, for, inasmuch as this must mean a decrease in the residual affinity of the NO_3-ions, such a decrease can only be brought about by a loose combination of these ions with the surrounding water molecules. In reference more particularly to the hydration at 45 per cent. of water, objection might be raised from the standpoint that such a hydrate would mean 250 molecules of water to one NO_3-ion, or, in other words, a hydrate of the composition $LiNO_3,250H_2O$. We, however, point out that there is no necessity for all the water molecules to take part in the reaction. In the reversible process

$$SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl,$$

a relatively great mass of water is required to carry out the hydrolysis, even although only one molecule is actually concerned for each $SbCl_3$ molecule. Similarly, in the reversible equation

$$LiNO_3 + xH_2O \rightleftarrows LiNO_3,xH_2O,$$

the value of x may be small relatively to the 250 molecules of water necessary for the hydration to take place. We may also point out that the hydrates which are known are those that are more or less stable in ordinary air; in the present case we are dealing with a hydrate only stable in the presence of a large mass of water, and there seems no valid reason why a deliquescent salt like lithium nitrate should not form a hydrate containing a large number of water molecules under the conditions specified. We therefore conclude that whilst ammonium and silver nitrates only form one hydrate, lithium nitrate forms one hydrate at 3 per cent. of water, and a second when the solvent contains about 45 per cent. of water.

We have also investigated nitric acid in absolute alcoholic solution and in solvents containing 3, 5, 10, and 25 per cent. of water respectively. The results are very interesting, owing to the fact that the $N/10$-solution in absolute alcohol is so little ionised. The method of preparing the solutions may perhaps be mentioned. A solution of silver nitrate stronger than $N/10$ was prepared in the required solvent. In the case of absolute alcohol, the solvent was mechanically shaken for some hours with an excess of the finely powdered salt, and the resulting solution was titrated. A solution of hydrogen chloride was also prepared by passing the dry gas into a second quantity of the solvent. This solution was also titrated, and equivalent volumes of the acid and silver solutions were mixed and mechanically shaken for some time in order to cause the silver chloride to coagulate and form a clear solution. This shaking usually took about half an hour to effect complete separation of the silver chloride. The resulting nitric acid solution was tested for excess of hydrochloric acid and silver nitrate, and, if both were absent, diluted with more of the appropriate solvent until exactly decinormal. The values of the conductivities are given, together with the persistences of the absorption band, in the following table:

TABLE III.

Nitric Acid. Temperature = 15°.

Percentage of water in solvent.	Mol. conductivity at $N/10$.	Limiting conductivity.	Percentage ionisation at $N/10$.	Persistence of absorption band.
0	4·428	42·6	10·4	3
0·5	6·00	—	—	7
3	15·22	38·7	39·3	30
5	19·62	—	—	40
10	27·85	42·5	65·27	70
25	47·52	—	—	110

and, as can be seen, although the conductivities of the $N/10$-solutions rapidly increase as water is added to the solvent, the limiting conductivities pass through the same minimum with 3 per cent. of water as in the case of lithium and ammonium nitrates. There is thus evidence that a similar hydration occurs. It is interesting to note that there is practically no absorption band exhibited by the absolute alcoholic solution of nitric acid, a fact which confirms Hartley's observation (*loc. cit.*) that the band is due to the ionised nitrate. With the rapid increase of ionisation caused by the increase in the water content of the solvent, the absorption band soon develops.

At Dr. Lapworth's suggestion, we have measured the conductivities of hydrogen chloride in a few solvents. The interest of this substance lies in the fact that $N/10$-solutions show a minimum conductivity with 0·5 per cent. of water in the solvent, which has been attributed to a decrease in the ionisation. Our results are given in the following table, and although we have been precluded from confirming the conclusion by absorption spectra observations (hydrogen chloride being quite diactinic), there is no doubt that a hydrate exists with 3 per cent. of water in the solvent, for the decrease in the limiting conductivity at this point is exceedingly pronounced.

TABLE IV.

Hydrogen Chloride at 15°.

Percentage of water in solvent.	Molecular conductivity at $N/10$.	Limiting conductivity.	Percentage of ionisation at $N/10$.
0	21·86	43·10	50·72
0·5	17·81	35·94	49·55
3	18·57	33·66	55·17
5	20·86	36·71	56·82
10	26·89	40·52	66·4
25	46·41	57·30	81·0

Although there is a small drop in the ionisation of the $N/10$-solution on the addition of 0·5 per cent. of water to the alcohol, it is evident that this is far from sufficient to account for the corresponding decrease in the conductivity of the $N/10$-solutions. From the decrease in the limiting conductivity at 0·5 per cent. of water, it is clear that the hydrogen chloride molecule must itself be considerably hydrated, and inasmuch as the ratio of water to hydrogen chloride molecules is about 3 to 1, it is not improbable that the hydrate, $HCl,3H_2O$, is formed. If that is so, it is not difficult to understand the decrease in ionisation of the $N/10$-solution at this point, for when no water is present the alcohol ionises the hydrogen chloride molecule, but when 0·5 per cent. of water is present, the alcohol has to ionise the compound $HCl,3H_2O$. In all probability, owing to the less free affinity of the hydrogen chloride in this case, the solvent will have greater difficulty in ionising the complex than in the case of the real hydrogen chloride molecule, where none of the residual affinity is satisfied by water molecules.

There is no doubt that these results with hydrogen chloride offer a very striking support to the theory of hydrogen ions put forward by Lapworth (Trans., 1908, **93**, 2187), for the values of the limiting conductivity show that the hydrogen and chlorine ions have much greater mobility in pure alcohol than when a little water is present; in other words, the presence of water alters their character, doubtless by hydration.

A point arises in connexion with the viscosity of the solvents, and the influence this may have on the values of the conductivity obtained. Walden (*Zeitsch. physikal. Chem.*, 1906, **55**, 217) has shown that in the case of tetramethylammonium iodide in various solvents, the product of the limiting conductivity and the viscosity of the solvent is constant. We have thought that a similar relation might hold good for lithium nitrate in the solvents employed in this investigation. No such constant, however, is obtained, as can be seen at once from the following table, in which the values of the viscosity are taken from Dunstan's paper (Trans., 1904, **85**, 824). Lithium nitrate appeared the most likely to give results agreeing with Walden's observations, since the limiting conductivities show a minimum at or about the point of maximum viscosity of the alcohol-water mixtures:

TABLE V.

Percentage of water in solvent.	Viscosity.	Limiting conductivity.	Product of viscosity and limiting conductivity.
0	0·01114	33·7	0·375
3	0·0120	32·2	0·386
5	0·0126	32·6	0·411
10	0·0142	31·9	0·453
25	0·0185	29·7	0·549
40	0·0225	28·0	0·629
50	0·0234	29·2	0·682
75	0·0195	42·2	0·823
100	0·0089	90·0	0·801

An interesting fact was noticed in making the absorption spectra observations, for it was found impossible, especially in the case of the solvents containing much alcohol, to recover the values of the persistence after the solution had been poured once or twice from one vessel to another. The persistence was always very considerably decreased, and it was eventually found that this decrease was due to the absorption of carbon dioxide from the air. The persistence of the absorption band is very sensitive, and when the solutions were saturated with carbon dioxide the band was very materially decreased in depth. The values of the limiting conductivity were also slightly reduced in the presence of this gas. It would therefore seem that the NO_3-ion has the power of forming loose additive compounds with carbon dioxide, and for this reason the solvents were always carefully freed from this gas before the solutions were made up.

We have to express our thanks to Dr. Lapworth and to Dr. Senter for the great interest they have taken in this investigation, and also to the Chemical Society for a grant in aid of the above experiments.

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CXXV.—*Studies in Asymmetric Synthesis. Part VIII. The Asymmetric Synthesis of* l-*Mandelic Acid.*

By **Alex. McKenzie** and **Herbert Brooke Perren Humphries**.

The first attempts made by one of us (Trans., 1904, **85**, 1249) to realise an asymmetric synthesis were not successful. The reduction of *l*-menthyl benzoylformate, $C_6H_5 \cdot CO \cdot CO_2 \cdot C_{10}H_{19}$, proceeded asymmetrically, since a mixture of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate containing a slight excess of the latter ester was obtained. This mixture, however, gave *r*-mandelic acid when it was saponified and the active menthol removed. It was found that this result was due to the racemising effect exercised by alcoholic potassium hydroxide, which was used to saponify the ester mixture (compare Trans., 1905, **87**, 1004; 1907, **91**, 1814).

The asymmetric synthesis of *l*-mandelic acid is described in the present communication. *l*-Menthyl benzoylformate was reduced by aluminium amalgam as before, the reduction product acetylated, and the mandelic acid obtained from the mixture of *l*-menthyl acetylmandelates by saponification and subsequent elimination of the menthol. The acid was lævorotatory, and the introduction of the acetyl group thus counteracted the racemising influence of the alkali to such an extent as to render an asymmetric synthesis possible.

The protecting effect of the acetyl group was observed first of all in connexion with some experiments dealing with the Walden inversion. The displacement of the acetyl group in *l*-acetylmandelic acid by the hydroxy-group by means of (1) water, (2) aqueous alkali, and (3) silver oxide in the presence of water was studied. As was expected, no Walden inversion occurred in these actions, doubtless since the acetyl group is not attached directly to the asymmetric carbon atom. The fractional saponification of *l*-menthyl *dl*-acetylmandelate was then investigated, and the observations made were so unexpected as to lead to the conclusion that a lævorotatory mandelic acid mixture should be obtainable by the complete saponification of the ester by a slight excess of alcoholic potassium hydroxide and subsequent removal of the menthol. This conclusion was borne out by experiment, and appears at first sight to invalidate the asymmetric synthesis of mandelic acid, to which reference has just been made. The evidence submitted in the experimental part of this paper proves, however, that the asymmetric synthesis in question had actually been effected.

Rosenthaler (*Biochem. Zeitsch.*, 1908, **14**, 238) has recently made the important discovery that *d*-benzaldehyde cyanohydrin can be synthesised by the action of emulsin on a mixture of hydrocyanic acid and benzaldehyde. The active cyanohydrin was hydrolysed, and *l*-mandelic acid isolated after two crystallisations of the resulting acid from benzene. The extent of the asymmetric synthesis effected by emulsin must accordingly have been very considerable, that is to say, there must have been a large preponderance of the *d*-cyanohydrin over the *l*-isomeride, otherwise the isolation of the pure *l*-mandelic acid could not have been possible in the manner described by Rosenthaler. It does not follow, however, that the pure *d*-cyanohydrin was synthesised free from the *l*-isomeride.

The asymmetric synthesis of *l*-mandelic acid has thus an additional interest when considered in connexion with Rosenthaler's work, because it is made clear how much more completely the asymmetric synthesis can be effected by enzyme action than by compounds of known constitution.

EXPERIMENTAL.

Displacement of the Acetyl Group in l-*Acetylmandelic Acid by the Hydroxy-group.*

l-*Acetylmandelic acid*, prepared from *l*-mandelic acid and acetyl chloride, crystallises from water in colourless needles. When dried in air at the ordinary temperature, it contains one molecule of water of crystallisation, which it loses slowly when exposed over sulphuric acid under diminished pressure at the ordinary temperature :

1·0471 lost 0·0896 H_2O. $H_2O = 8·6$.

$C_{10}H_{10}O_4,H_2O$ requires $H_2O = 8·5$ per cent.

The anhydrous acid melts, not very sharply, at 96·5—98°. It undergoes slight decomposition when heated at 90—100°. A brief reference to the acid is made by Walden (*Zeitsch. physikal. Chem.*, 1895, **17**, 706), who gives m. p. 56° and $[\alpha]_D$ $-156·4°$ in acetone. The rotation of the anhydrous acid was determined by us in ethyl-alcoholic solution :

$$l = 2, c = 2·22, \alpha_D^{15} -7·00°, [\alpha]_D^{15} -157·7°.$$

and in acetone :

$$l = 2, c = 2·085, \alpha_D^{15} -6·41°, [\alpha]_D^{15} -153·7°.$$

The anhydrous acid is sparingly soluble in water, carbon tetrachloride, or light petroleum, moderately so in benzene, and readily so in ethyl alcohol, methyl alcohol, ether, chloroform, or acetone :

0·4309 required 13·9 c.c. of cold ethyl-alcoholic potassium hydroxide (1 c.c. = 0·009 KOH) for neutralisation.

$C_{10}H_{10}O_4$ requires 13·85 c.c.

0·884 was boiled for forty-five minutes with excess of 0·398*N*-alcoholic potash, the excess being estimated by titration against standard acid ; required 22·9 c.c. alkali :

$C_{10}H_{10}O_4$ requires 22·9 c.c.

The hydrated acid (0·53 gram) was boiled with water (50 c.c.) for fifteen and a-half hours. The resulting mandelic acid gave $[\alpha]_D$ $-145°$ for $c = 1·7$ in aqueous solution, whereas the value of the specific rotation of *l*-mandelic acid is about 12° higher than this. A little racemisation had thus occurred.

The anhydrous acid (0·916 gram) was boiled for one hour with 35·5 c.c. of 0·39*N*-alcoholic potash. The resulting mandelic acid had $[\alpha]_D^{14}$ $-148°$ for $c = 1·7$ in ethyl-alcoholic solution, whereas the *l*-acid under similar conditions has $[\alpha]_D$ $-157°$.

When the anhydrous acid (0·5 gram) was boiled for two and a-quarter hours with 30 c.c. of *N*/5-aqueous sodium hydroxide, no appreciable racemisation took place. Practically pure *l*-mandelic acid was also recovered when the acetyl group was removed by the aid of silver oxide and water. No Walden inversion was thus observed.

Fractional Esterification of r-*Acetylmandelic Acid by Optically Active Alcohols.*

The method of Marckwald and McKenzie (*Ber.*, 1899, **32**, 2130 ; 1900, **33**, 208 ; 1901, **34**, 469) was used. Ten grams of *r*-acetylmandelic acid, m. p. 79—80° (compare Böcker, *Inaug. Diss.*, Bonn,

1905) were heated with *l*-menthol (10 grams) for one hour at 150°. The unesterified acid was separated from menthol and menthyl esters, and consisted of a mixture of mandelic and acetylmandelic acids. It amounted to 7·4 grams, and was dextrorotatory, giving $[\alpha]_D +2·5°$ for $c=8·85$ in ethyl-alcoholic solution. The ester mixture was saponified by heating with a solution of 5·6 grams of potassium hydroxide in 80 c.c. of ethyl alcohol for one and a-half hours, the alkali being thus present in excess. The mandelic acid, obtained in the usual manner, amounted to 1·67 grams, and was lævorotatory, giving $[\alpha]_D -9·3°$ for $c=7·87$ in ethyl-alcoholic solution.

The conclusion may thus be drawn that *l*-acetylmandelic acid is esterified by *l*-menthol more quickly than is *d*-acetylmandelic acid.

It accordingly appeared from this experiment that, whilst the racemisation which takes place during the saponification of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate respectively is very considerable (Trans., 1904, **85**, 378, 1249), this racemisation may be largely prevented by the introduction of the acetyl group into the menthyl esters.

The fractional esterification of *r*-acetylmandelic acid by the active borneols was also examined. The acid (10 grams) was heated at 150° for one and a-quarter hours with *l*-borneol (10 grams). The unesterified acid, which was completely separated from borneol and bornyl esters, amounted to 3·83 grams, and was lævorotatory, giving $[\alpha]_D -7·9°$ for $c=10·97$ in ethyl-alcoholic solution. This acid contained very little acetylmandelic acid, the acetyl group having been eliminated almost completely in the process of separation of the acid. The ester mixture was saponified by boiling for seventy minutes with a solution of 6·25 grams of potassium hydroxide in 80 c.c. of ethyl alcohol. The mandelic acid recovered (4·1 grams) was dextrorotatory, giving $[\alpha]_D +1·7°$ for $c=10·19$ in ethyl-alcoholic solution.

This experiment showed that: (1) esterification takes place more quickly when *l*-borneol is substituted for *l*-menthol; (2) *d*-acetylmandelic acid is esterified more quickly by *l*-borneol than is *l*-acetylmandelic acid, and (3) racemisation during the saponification of the ester mixture is more pronounced in this case than with *l*-menthol, but not so pronounced as when the menthyl mandelates are saponified.

These deductions were confirmed by a similar experiment, where the same quantities of the *r*-acid and *d*-borneol were used. The heating was conducted for one hour. The unesterified acid (4·15 grams) was dextrorotatory, giving $[\alpha]_D +6·6°$ for $c=10·61$ in ethyl-alcoholic solution. The saponification of the ester mixture was conducted by boiling for one hour with a solution of 5·68 grams of potassium hydroxide in 80 c.c. of ethyl alcohol. The recovered mandelic acid (3·67 grams) was lævorotatory, giving $[\alpha]_D -2·1°$ for $c=10·43$ in ethyl-alcoholic solution.

Fractional Saponification of l-*Menthyl* dl-*Acetylmandelate.*

Thirty grams of *l*-menthyl *r*-mandelate (Trans., 1904, **85**, 378) were warmed with an excess of acetyl chloride for one hour. The excess of acetyl chloride was removed under diminished pressure, and the residual oil distilled.

l-*Menthyl* dl-*acetylmandelate*, $C_6H_5{\cdot}CH(OAc){\cdot}CO_2{\cdot}C_{10}H_{19}$, is a colourless oil, which boils at 205°/7 mm. For analysis, it was heated with an excess of standard alcoholic potassium hydroxide for one and a-half hours, the excess of alkali being then estimated by standard acid :

1·4415 required 22·3 c.c. alkali (0·39*N*).

$C_{20}H_{28}O_4$ requires 22·3 c.c.

Determinations of its specific rotation in ethyl-alcoholic solution gave :

$$l = 2,\ c = 9{\cdot}128,\ \alpha_D^{13{\cdot}5} - 10{\cdot}41°,\ [\alpha]_D^{13{\cdot}5}\ - 57{\cdot}0°.$$
$$l = 2,\ c = 2{\cdot}5325,\ \alpha_D^{14}\ - 2{\cdot}90°,\ [\alpha]_D^{14}\ - 57{\cdot}2°.$$

Initial Saponification.—The ester (6 grams) was dissolved in 33 c.c. of 0·39*N*-alcoholic potassium hydroxide, this being about one-third of the amount required for saponification and elimination of the acetyl group. After twenty-four hours at the ordinary temperature, the alcohol was evaporated, water added, and the mixture concentrated a little by evaporation on the water-bath. It was rendered alkaline by sodium hydroxide, and the menthol and unsaponified esters removed by extraction with ether and subsequent evaporation of the aqueous solution. The latter was acidified by mineral acid, and the mandelic acid extracted with ether. The acid (0·81 gram) was dextrorotatory, giving $[\alpha]_D + 15{\cdot}4°$ for $c = 3{\cdot}92$ in ethyl-alcoholic solution.

Final Saponification.—The mixture of unsaponified esters was then heated for two hours with 30 c.c. of 0·39*N*-ethyl-alcoholic potassium hydroxide, an amount which was found to be sufficient for complete saponification. During the initial saponification, the acetyl groups must therefore have been eliminated very considerably from the residual acetyl esters. A large excess of alkali was avoided on purpose during the final saponification, in order to minimise the racemisation. The alkaline solution was acidified by a little dilute hydrochloric acid, the alcohol expelled, and the menthol removed in the usual manner. The mandelic acid obtained (1·5 grams) was lævorotatory, giving $[\alpha]_D - 14{\cdot}5°$ for $c = 7{\cdot}31$ in ethyl-alcoholic solution.

Now it has been shown that of the two esters, *l*-menthyl *d*-acetylmandelate and *l*-menthyl *l*-acetylmandelate, the latter is the more quickly formed ; it ought, therefore, to be the more quickly saponifiable. The fractional saponification of *l*-menthyl *dl*-acetylmandelate, which in alcoholic solution is doubtless split up into the diastereoisomeric esters,* might therefore be expected to give a lævorotatory mandelic acid mixture as the product of the initial saponification. It will be observed from the experiment just described, that the acid from the initial saponification is dextrorotatory. It has been shown, however (Trans., 1905, **87**, 1004; 1907, **91**, 1814), that during the fractional saponification of *l*-menthyl *r*-mandelate, the racemisation caused by the alkali in the early stages of the saponification is marked, but becomes less and less so as the saponification proceeds. It was further shown that, by variation of the experimental conditions, it is possible to obtain at will either a dextrorotatory or a lævorotatory mandelic acid mixture from the initial saponification of *l*-menthyl *r*-mandelate, although it has been proved by direct measurements of the velocity of saponification (Trans., 1907, **91**, 789) that *l*-menthyl *d*-mandelate is saponified more quickly than is *l*-menthyl *l*-mandelate. An interpretation on similar lines to that given formerly may be advanced to account for this abnormal result on the fractional saponification of the *dl*-acetyl ester. But the present case is more complicated than the former one, since an additional factor is introduced, namely, the elimination of the acetyl group. Since *l*-menthyl *d*-acetylmandelate and *l*-menthyl *l*-acetylmandelate are not enantiomorphously related, the velocity of displacement of the acetyl group in each of these esters is probably not the same. Again, in the present case, the racemising effect of alkali is less than when *l*-menthyl *r*-mandelate is saponified under similar conditions, since the alkali is partly used up to fix the acetyl groups as potassium acetate, and there is less of it available for racemisation.

The striking feature in the experiment quoted is, however, the preponderance of *l*-mandelic acid formed. The theoretical amount of mandelic acid obtainable from 6 grams of *l*-menthyl *dl*-acetylmandelate is 2·78 grams, whereas 2·31 grams were actually obtained, the initial saponification giving 0·81 gram with $[\alpha]_D$ +15·4°, and the final saponification 1·5 grams with $[\alpha]_D$ −14·7°.

In a second experiment, *l*-menthyl *dl*-acetylmandelate (6·3 grams) was boiled with 30·5 c.c. of 0·39*N*-alcoholic potassium hydroxide; the solution was neutral after two minutes. The acid obtained as before amounted to 0·8 gram, and had $[\alpha]_D$ +8·7° for $c = 3·8$ in ethyl-alcoholic solution. The ester mixture was dissolved in 75 c.c. of 0·39*N*-alcoholic potassium hydroxide, and allowed to remain for three weeks at the ordinary temperature. The resulting mandelic acid (1·81 grams) gave $[\alpha]_D$ −13·2° for $c = 9·0$ in ethyl-alcoholic solution. The theoretical amount of mandelic acid obtainable from 6·3 grams of ester is 2·88 grams; the amount obtained was 2·61 grams.

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* Compare, however, Kipping (this vol., 408), who deals with the question of the existence of partially racemic salts in solution.

In another experiment, 4·75 grams of ester were dissolved in 49 c.c. of 0·39*N*-alkali, an amount which is two-thirds of that necessary for complete saponification of the ester and elimination of the acetyl group. After two days at the ordinary temperature, the solution was neutral. The resulting acid had $[\alpha]_{\mathrm{D}}$ +10·1° for $c = 6{\cdot}46$ in ethyl-alcoholic solution. The ester mixture was saponified at the ordinary temperature by 26·5 c.c. of alkali, which was more than was necessary. The resulting acid had $[\alpha]_{\mathrm{D}}$ −30·7° for $c = 2{\cdot}37$ in ethyl-alcoholic solution.

It need hardly be stated that the necessary precautions were taken to ensure that the mandelic acid mixtures, which were polarimetrically examined in these experiments, were free from menthol.

The deduction was drawn that a *laevorotatory* mandelic acid mixture might be obtained from *l*-menthyl *dl*-acetylmandelate by acting on it with an *excess* of alkali and then removing the menthol. This was found to be the case (see later).

It was therefore necessary to show that this curious result was not due to the *l*-menthyl *dl*-acetylmandelate containing a little excess of the *l*-menthyl *l*-acetylmandelate, and the following evidence is accordingly submitted.

(1) l-*Menthyl* l-*acetylmandelate*, $C_6H_5{\cdot}CH(OAc){\cdot}CO_2{\cdot}C_{10}H_{19}$, was prepared by acetylating *l*-menthyl *l*-mandelate (Trans., 1904, **85**, 1249) with acetyl chloride. It is readily soluble in ether, ethyl alcohol, benzene, carbon tetrachloride, light petroleum, carbon disulphide, methyl acetate, chloroform, or heptane, and sparingly so in water. It crystallises from aqueous alcohol in colourless needles and melts at 45—46°:

1·0305 required 15·6 c.c. of 0·399*N*-ethyl-alcoholic potassium hydroxide for elimination of the acetyl and menthyl groups.

$C_{20}H_{28}O_4$ requires 15·55 c.c.

Its rotation was determined in ethyl-alcoholic solution:

$$l = 2,\ c = 2{\cdot}584,\ \alpha_{\mathrm{D}}^{9\cdot5} - 6{\cdot}36°,\ [\alpha]_{\mathrm{D}}^{9\cdot5}\ - 123{\cdot}1°.$$

l-*Menthyl* d-*acetylmandelate*, $C_6H_5{\cdot}CH(OAc){\cdot}CO_2{\cdot}C_{10}H_{19}$, prepared by acetylating *l*-menthyl *d*-mandelate (Trans., 1904, **85**, 1249) with acetyl chloride, crystallises from aqueous alcohol in needles and melts at 44·5—45°:

1·0067 required 16·0 c.c. of 0·378*N*-ethyl-alcoholic potassium hydroxide.

$C_{20}H_{28}O_4$ requires 16·0 c.c.

Its rotation was determined in ethyl-alcoholic solution:

$$l = 2,\ c = 2{\cdot}679,\ \alpha_{\mathrm{D}}^{12}\ +0{\cdot}47°,\ [\alpha]_{\mathrm{D}}^{12}\ +8{\cdot}8°.$$

The rotations of the three isomeric *l*-menthyl acetylmandelates were taken under similar conditions of concentration and temperature.

The value $[\alpha]_D$ $-57·15°$, calculated for *l*-menthyl *dl*-acetylmandelate from the preceding results, is practically identical with that actually found, namely $-57·2°$.

(2) The saponification of *l*-menthyl *d*-acetylmandelate and *l*-menthyl *l*-acetylmandelate respectively under similar conditions was studied. A solution of the former ester (1·0067 grams) in 17·64 c.c. (calculated, 16·0 c.c.) of 0·378*N*-ethyl-alcoholic potassium hydroxide was kept at the ordinary temperature for twenty-three hours, and was then boiled gently for ten minutes. The mandelic acid, extracted in the usual manner after the removal of the menthol, had $[\alpha]_D$ $+86·6°$ for $c=3·94$ in aqueous solution. (*d*-Mandelic acid has $[\alpha]_D$ about $+158°$ under similar conditions.) A parallel experiment was carried out at the same time with *l*-menthyl *l*-acetylmandelate. The mandelic acid recovered in this case gave $[\alpha]_D -94·7°$ for $c=4·1$ in aqueous solution.

(3) The *l*-menthyl *dl*-acetylmandelate described in this paper had $[\alpha]_D^{14}$ $-57·2°$ for $c=2·5325$ in ethyl-alcoholic solution. In its preparation vacuum distillation was resorted to. This ester may be regarded as a mixture in equal amounts of *l*-menthyl *d*-acetylmandelate and *l*-menthyl *l*-acetylmandelate, and it is quite conceivable that at elevated temperatures these esters can undergo partial optical inversion with different velocities in the acetylmandelic portion of their molecules, the menthyl portion remaining optically unchanged. The effect of the vacuum distillation might therefore be to give a mixture of unequal amounts of the two diastereoisomeric esters. That such is not the case was shown by the following observation.

l-Menthyl *d*-acetylmandelate (0·1260 gram) and *l*-menthyl *l*-acetylmandelate (0·1260 gram) were mixed, and the oil which was formed on warming was dissolved in ethyl alcohol. The following rotation was taken:

$$l=2,\ c=2·52,\ \alpha_D^{13·5}\ -2·885°,\ [\alpha]_D^{13·5}\ -57·2°.$$

This value is identical with that given above.

l-*Menthyl Benzoylmandelates.*

l-*Menthyl* dl-*benzoylmandelate*, $C_6H_5·CH(OBz)·CO_2·C_{10}H_{19}$, prepared by benzoylating *l*-menthyl *r*-mandelate by the Schotten-Baumann method, separates from ethyl alcohol in flat, glassy needles and melts at 75—76°:

1·4989 required 19·05 c.c. of 0·399*N*-ethyl-alcoholic potassium hydroxide for elimination of the benzoyl and menthyl groups.

$C_{25}H_{30}O_4$ requires 19·06 c.c.

Its specific rotation in ethyl-alcoholic solution was determined:

$$l=2,\ c=3·984,\ \alpha_D^{23}\ -3·54°,\ [\alpha]_D^{23}\ -44·4°.$$

The fractional saponification of this ester was accompanied by a considerable amount of racemisation. In one experiment, 4·1 grams were saponified at the ordinary temperature by half the calculated amount of alkali; the mandelic acid resulting from this initial saponification, after separation from menthol and benzoic acid, amounted to 1·2 grams, and had $[\alpha]_D$ $-2·5°$ in ethyl-alcoholic solution. The residual esters on saponification gave a mandelic acid (0·24 gram) with $[\alpha]_D$ $-33·7°$. The total mandelic acid obtained was thus 1·44 grams, the theoretical amount being 1·58 grams.

In another experiment, where one-third of the calculated amount of alkali was used for the initial saponification, the resulting mandelic acid was dextrorotatory, giving $[\alpha]_D$ $+3·6°$, whereas the final saponification gave an acid with $[\alpha]_D$ $-29·0°$.

It was thus clear that benzoylation would be of little value as an aid towards realising the asymmetric synthesis of mandelic acid. That the racemisation was very pronounced during saponification was also shown by the behaviour of *l*-menthyl *l*-benzoylmandelate (Trans., 1904, **85**, 1249) towards ethyl-alcoholic potassium hydroxide. The mandelic acid obtained had $[\alpha]_D$ $-39·2°$ in aqueous solution.

Asymmetric Synthesis of l-*Mandelic Acid.*

The reduction of *l*-menthyl benzoylformate, $C_6H_5·CO·CO_2·C_{10}H_{19}$, was described in a former paper (*loc. cit.*). In one case, the reduced product had $[\alpha]_D$ $-76·9°$ in ethyl-alcoholic solution, and in another case it had $[\alpha]_D$ $-77·6°$. Since *l*-menthyl *r*-mandelate has $[\alpha]_D$ about $-74°$, the product of the reduction of the benzoylformate contained a slight preponderance of *l*-menthyl *l*-mandelate. In the present experiments the reduction product was slightly more active than formerly.

Experiment I.—*l*-Menthyl benzoylformate (3 grams) was reduced by aluminium amalgam. The menthyl mandelate formed gave the following value for the specific rotation in ethyl-alcoholic solution.

$$l=2,\ c=2·952,\ \alpha_D^{18·5}\ -4·81°,\ [\alpha]_D^{18·5}\ -81·5°.$$

This product was acetylated by acetyl chloride, the excess of the latter evaporated, and the residue kept under diminished pressure until the odour of acetyl chloride had disappeared. The residual viscous liquid (3·09 grams) was dissolved in 52·5 c.c. of 0·399*N*-ethyl-alcoholic potassium hydroxide to which one c.c. of water had been added. The theoretical amount of alkali necessary for the displacement of the acetyl and menthyl groups is 46·7 c.c. After twenty-two hours at the ordinary temperature, the alkaline solution was boiled for five minutes, and then nearly neutralised by mineral acid. Water was added, and the solution heated for some time to expel the bulk of the ethyl alcohol. The menthol was then completely removed in the usual manner by extraction with ether and subsequent evaporation of the aqueous solution. The mandelic acid mixture, obtained by acidification and extraction with ether, amounted to 1·2 grams, the theoretical amount being 1·4 grams. It melted at 114—119°, and gave the following result on polarimetric examination in aqueous solution:

$$l=4,\ c=4{\cdot}4,\ \alpha_{\mathrm{D}}^{12\cdot5}\ -2{\cdot}74^{\circ},\ [\alpha]_{\mathrm{D}}^{12\cdot5}\ -15{\cdot}6^{\circ}.$$

This result shows definitely that an asymmetric synthesis had taken place, since the activity of the mandelic acid, formed by the complete saponification of *l*-menthyl *dl*-acetylmandelate where a large excess of alkali was avoided, is much less than $[\alpha]_{\mathrm{D}}\ -15{\cdot}6^{\circ}$. *l*-Menthyl *dl*-acetylmandelate (2 grams) was dissolved in 34·5 c.c. of ethyl-alcoholic potassium hydroxide (0·398*N*), the calculated amount being 30·3 c.c. After two days at the ordinary temperature, the mixture was boiled for ten minutes, the alkalinity reduced by mineral acid until the solution was nearly neutral, the menthol removed as usual, and the mandelic acid recovered. The acid had the following rotation in aqueous solution:

$$l=2,\ c=3{\cdot}4145,\ \alpha_{\mathrm{D}}^{17}\ -0{\cdot}20^{\circ},\ [\alpha]_{\mathrm{D}}^{17}\ -3{\cdot}1^{\circ}.$$

A lævorotatory mandelic acid was also obtained by boiling the ester for twenty minutes immediately after solution in the alkali, which, as before, was used in excess.

Experiment II.—*l*-Menthyl benzoylformate (3 grams) was reduced in much the same manner as formerly by means of aluminium amalgam. The resulting mandelate gave on polarimetric examination in ethyl-alcoholic solution:

$$l=2,\ c=3{\cdot}223,\ \alpha_{\mathrm{D}}^{15}\ -5{\cdot}17^{\circ},\ [\alpha]_{\mathrm{D}}^{15}\ -80{\cdot}2^{\circ}.$$

The ester was acetylated, and 2·5 grams of the product dissolved in 44 c.c. of 0·378*N*-ethyl-alcoholic potassium hydroxide, the calculated amount being 39·8 c.c. A 10 per cent. excess of alkali was thus used. The solution was boiled for twenty minutes, and the mandelic acid isolated in the usual manner. The activity was determined in aqueous solution:

$$l=4,\ c=3{\cdot}9224,\ \alpha_{\mathrm{D}}^{19}\ -1{\cdot}71^{\circ},\ [\alpha]_{\mathrm{D}}^{19}\ -10{\cdot}9^{\circ}.$$

l-Menthyl *dl*-acetylmandelate was saponified under conditions similar to the preceding.

The ester (2·06 grams) was dissolved in 36 c.c. of 0·378*N*-alkali, a 10 per cent. excess. The mandelic acid recovered had the following rotation in aqueous solution:

$$l=2,\ c=4{\cdot}2275;\ \alpha_{\mathrm{D}}^{13\cdot5}\ -0{\cdot}38^{\circ},\ [\alpha]_{\mathrm{D}}^{18\cdot5}\ -4{\cdot}5^{\circ}.$$

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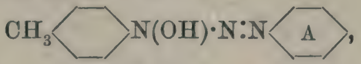
CXXVI.—*Diazohydroxylamino-compounds and the Influence of Substituting Groups on the Stability of their Molecules. Part II.*

By Norman Leslie Gebhard and Herbert Bryan Thompson.

In a previous communication (this vol., p. 767), a number of diazohydroxylamino-compounds were described, all of which might be considered as mono-substitution products of the parent substance, benzenediazohydroxylamino-*p*-toluene,



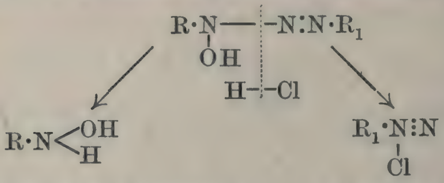
and containing their various substituting groups in the ring A in various positions relative to the azo-grouping already present. The object of the present paper is to describe experiments carried out with a view to determine the influence of these various substituting groups on the general stability of the molecule. The problem was attacked in two ways: first, the action of bromine dissolved in an organic solvent was tried, and secondly, the effect of treating each separate compound with an acid under definite conditions of temperature and concentration, that is, under known conditions, was determined.

The Action of Bromine in Chloroform Solution.

The initial experiments on the action of bromine in chloroform solution on these substances seemed, at the outset, to lead to the general conclusion that the method would form an excellent means of obtaining a qualitative idea of the stability of the various compounds on which it was tried, and hence information as to the effect produced by the various substituting groups on the stability of the molecule containing them. A closer examination, however, of the reaction revealed the fact that, not only did bromine act as a decomposing agent towards the compound in question, but that it also acted as a substituting agent, and that both these processes took place at one and the same time in the case of some of the compounds concerned, whilst in the case of others, the one or the other took place as the case might be; as a consequence of this, the action of bromine could hardly be considered as one throwing any great light on the object in view. In consideration, however, of the fact that some few new diazohydroxylamino-compounds were isolated by this means, and that in general the results of the action are in keeping, at least in degree with those obtained by the second or better method, it was determined to quote this work in some detail, and the results derived from it will be found in the experimental part.

The Action of Hydrochloric Acid on the Diazohydroxylamino-compounds.

As was previously shown (*loc. cit.*), all diazohydroxylamino-compounds are affected by hydrochloric acid, which apparently is much more powerful when acting in solution in an organic solvent. The decomposing action of this acid is a very simple one, as may readily be proved by qualitative means: a diazonium compound and a hydroxylamine (or a product of its rearrangement) results thus:



A hydroxylamine (which necessarily suffers subsequent rearrangement under the influence of the acid).

A diazonium salt.

This decomposing action was now made use of as a means of ascertaining quantitatively how much of each separate diazohydroxylamino-compound was decomposed when treated with the acid under as comparable conditions as possible. The method used consisted in allowing the acid, in definite quantity at a suitable concentration and at a definite temperature, to act on the variously substituted diazohydroxylamino-compounds for definite lengths of time, in order to determine exactly in each case what effect ortho-substitution has over and above para- and meta-substitution, and, furthermore, to derive, where possible, any information respecting the relative effects of each specific substituting group on the stability of the molecule. Dealing, as is obvious, with a whole series of compounds all possessing different solubilities in various solvents, it was hardly possible to lay down any definite conditions to be observed throughout. The factor, temperature, at which the decompositions were carried out was, however, fixed at 15°, and owing to the different solubilities shown by the various substances, all experiments could not be carried out in the same solvent. A further difference in the examination of the various substances which it was necessary to observe was occasioned by the wide differences existing between the ease with which some were decomposed and others not, necessitating the use of varying amounts of hydrochloric acid compatible with experimental exactness.

A known amount of the substance to be examined, namely, 0·25 gram, was dissolved in a definite quantity in the organic solvent (either chloroform or glacial acetic acid), and to it was added a definite volume of the same solvent saturated with dry hydrogen chloride at 15°. The mixture was kept at 15° for a definite time, when it was treated in such a manner as to isolate in aqueous solution the diazonium compound formed, the actual amount of the same being estimated by treatment at the boiling point with 2*N*-sulphuric acid, the nitrogen evolved being collected. From the volume, temperature, and pressure of the gas obtained, it was an easy matter to determine the actual amount of the diazohydroxylamino-compound decomposed under the conditions employed.

A series of experiments was carried out on the variously substituted diazohydroxylamino-compounds on the above lines, the results of which are tabulated below.

Substance.	Solution.	Composition of decomposing solution.	Duration of experiment in hours.	Dry nitrogen at N.T.P. obtained in c.c.	Percentage decomposition.
Benzenediazohydroxylamino-*p*-toluene.	$CHCl_3$	15 c.c. $CHCl_3$ 15 c.c. $CHCl_3$ (saturated with HCl)	22	17·9	72·6
o-Bromobenzenediazohydroxylamino-*p*-toluene.	$CHCl_3$	15 c.c. $CHCl_3$ 15 c.c. $CHCl_3$ (saturated with HCl)	22	6·48	35·4
p-Bromobenzenediazohydroxylamino-*p*-toluene.	$CHCl_3$	15 c.c. $CHCl_3$ 15 c.c. $CHCl_3$ (saturated with HCl)	22	11·5	62·8
m-Bromobenzenediazohydroxylamino-*p*-toluene.	$CHCl_3$	15 c.c. $CHCl_3$ 15 c.c. $CHCl_3$ (saturated with HCl)	22	16·36	89·4
o-Tolyldiazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	30 c.c. $C_2H_4O_2$ 10 c.c. $C_2H_4O_2$ (saturated with HCl)	2	7·68	32·4
p-Tolyldiazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	30 c.c. $C_2H_4O_2$ 10 c.c. $C_2H_4O_2$ (saturated with HCl)	2	11·79	49·8
m-Tolyldiazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	30 c.c. $C_2H_4O_2$ 10 c.c. $C_2H_4O_2$ (saturated with HCl)	2	6·38	26·9
o-Nitrobenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	3·55	16·3
p-Nitrobenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	13·44	61·92
m-Nitrobenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	10·98	50·6
o-Carbethoxybenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	2·54	13·5
p-Carbethoxybenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	6·79	36·3
m-Carbethoxybenzenediazohydroxylamino-*p*-toluene.	$C_2H_4O_2$	20 c.c. $C_2H_4O_2$ (saturated with HCl)	12	9·07	48·4

NOTE.—0·25 gram was used in each case. Temperature 15°.

Discussion of Results.

The main fact to be deduced from the foregoing series of experiments is that when a diazohydroxylamino-compound is substituted by some group or other in the ortho-position relative to the one occupied by the azo-group, then the general stability of the molecule is sensibly increased. In other words, the effect of an ortho-substituent on the action of decomposing agencies is a protective one; it may, in fact, be compared with that similar phenomenon shown by the esters of differently substituted aromatic acids towards hydrolysis, when, as is well known, the presence of a substituent grouping in the ortho-position with respect to the carboxyl group greatly retards the same (compare V. Meyer and A. M. Kellas, *Zeitsch. physikal. Chem.*, 1897, **24**, 243; *Ber.*, 1895, **28**, 1258). Similar phenomena are also observed in the behaviour of aromatic amines when similarly substituted relative to the amino-group (compare A. Werner, *Lehrbuch der Stereochemie*). The protective influence, as it has been termed, which substituents in the ortho-position relative to the azo-group exert on the stability of the molecules of these diazohydroxylamino-compounds towards decomposing influences, from analogy may therefore be said to be further examples of the well-known phenomenon of steric hindrance.

A much better idea of the differences existing in the decomposability of isomeric compounds containing their substituting group in the ortho-, para-, and meta-positions respectively can be gained by a glance at the foregoing table. With the exception of the methyl substituted derivatives, it will readily be observed that the ortho-compounds all show the least amount of decomposition compared with that of their para- and meta-isomerides respectively, the decomposing influences, it will be noted, being identical in the case of each set of isomerides.

The hindering influence against decomposition exerted by groups situated in the ortho-position with respect to the azo-group in these compounds is therefore amply demonstrated, and is quite comparable with other well-known cases of steric hindrance. A comparison of the influence of the various substituting groups themselves on the stability of the substances regarding the question as to which exercises the greatest hindering effect cannot be entered into by reason of the fact that although the decomposing influences made use of are comparable for any three isomeric substances, yet these influences, naturally changed for reasons before stated, are in no way comparable where substances containing different substituting groups are concerned.

The results obtained from the action of bromine on these diazohydroxylamino-compounds, which are of interest as throwing a light on the problems, will be found detailed with each specific reaction noted.

EXPERIMENTAL.

*Action of Bromine in Chloroform Solution on Benzenediazohydroxylamino-*p*-toluene.*

A solution of 0·45 gram of benzenediazohydroxylamino-*p*-toluene in 15 c.c. of chloroform was mixed with 6·4 c.c. of a 10 per cent. solution of bromine, also in chloroform at 10°. After rapidly reducing the slight rise in temperature produced, the mixture was kept for ten minutes, and the crystals which separated were collected; these were proved qualitatively to consist of a bromo-substitution product of the original substance. The chloroform mother liquor was extracted thoroughly with water, and the aqueous extract on testing with an alkaline solution of β-naphthol was found to contain the merest trace of a diazonium compound. On evaporation of the chloroform solution, a few pale brown crystals separated, and a very faint odour of a nitroso-compound was noticeable. Under the above conditions the action of bromine appears to be almost entirely one of substitution, practically no fission of the molecule taking place.

*Action of Bromine in Chloroform Solution on the Methyl Derivatives of Benzenediazohydroxylamino-*p*-toluene.*

(*a*) o-*Tolyldiazohydroxylamino*-p-*toluene.*—A chloroform solution of the above compound was treated with two molecular proportions of bromine; a considerable rise in temperature took place, and, after keeping for ten minutes at 18°, the solution was extracted with water and the chloroform evaporated in a vacuum. A semi-crystalline residue was left, which, after drying on a porous plate, was recrystallised:

0·1275 gave 14·7 c.c. N_2 at 21° and 758 mm. N = 13·09.
0·1375 „ 0·0796 AgBr. Br = 24·95.
$C_{14}H_{14}ON_3Br$ requires N = 13·13; Br = 25·00 per cent.

The reactions of this substance are almost identical with those of the diazohydroxylamino-compound from which it is derived, and it is thus a *monobromo*-o-*tolyldiazohydroxylamino*-p-*toluene.*

It melts at 120·5°, and crystallises in stumpy, broad, flat needles of a fine yellow colour, which turn brown on exposure to light and air. It is very readily soluble in benzene, chloroform, and acetone, but more sparingly so in alcohol, ether, or light petroleum.

From the porous plate on which the crude bromination product was dried, a small quantity of a bright green oil, showing all the properties of, and being identical with, *p*-nitrosotoluene, was isolated.

On adding the aqueous extract of the chloroform solution to an alkaline solution of β-naphthol, a considerable quantity of a deep scarlet dye (*bromo*-o-*tolylazo-β-naphthol*) was precipitated, which, on crystallisation from glacial acetic acid, melted at 171°:

0·1563 gave 0·0850 AgBr. Br = 23·14.

$C_{17}H_{13}ON_2Br$ requires Br = 23·46 per cent.

Bromine thus apparently exercises primarily a substituting influence, the substituted product subsequently suffering decomposition.

(*b*) m-*Tolyldiazohydroxylamino*-p-*toluene*.—By a similar action of bromine in chloroform solution this compound yielded *monobromo*-m-*tolyldiazohydroxylamino*-p-*toluene*, which melts at 155° and crystallises in bright yellow, long, slender, hair-like needles; these are very sparingly soluble in light petroleum or alcohol, more readily so in benzene, ether, or acetone, and very readily so in chloroform:

0·1125 gave 12·7 c.c. N_2 at 20·5° and 762 mm. N = 12·93.
0·1341 „ 0·0794 AgBr. Br = 25·19.

$C_{14}H_{14}ON_3Br$ requires N = 13·3; Br = 25·00 per cent.

The substance is very much more stable than the diazohydroxylamino-compound from which it is derived, otherwise the reactions of the two substances are almost identical.

A bright scarlet dye (*bromo*-m-*tolylazo-β-naphthol*) was obtained from the aqueous extract of the chloroform solution, and, when pure, melted at 145°:

0·1271 gave 0·0696 AgBr. Br = 23·30.

$C_{17}H_{13}ON_2Br$ requires Br = 23·46 per cent.

Hence the action of bromine in this case is practically identical with that obtained from the ortho-isomeride.

(*c*) p-*Tolyldiazohydroxylamino*-p-*toluene*.—In this case also the action of bromine gave rise to a *monobromo*-substitution product, which crystallises in long, slender, bright yellow needles melting at 102°. With the exception of alcohol and light petroleum, the substance is very readily soluble in the common organic solvents:

0·1131 gave 0·0670 AgBr. Br = 25·20.

$C_{14}H_{14}ON_3Br$ requires Br = 25·00 per cent.

Its reactions are practically identical with those of the compound from which it is derived.

A considerable quantity of *p*-nitrosotoluene was also isolated as a result of the reaction, and the bright red dyestuff obtained by coupling the diazonium salt obtained from the aqueous extract of the original reaction mixture with β-naphthol was found to be identical with *p*-tolylazo-β-naphthol, and thus to contain no bromine, differing in this respect from the dyes obtained in the case of the ortho- and meta-isomerides. Bromine thus has not only a substituting action, but also a decomposing one, both apparently taking place simultaneously.

*Action of Bromine in Chloroform Solution on the Carbethoxybenzenediazohydroxylamino-*p*-toluenes.*

(*a*) o-*Carbethoxybenzenediazohydroxylamino*-p-*toluene.*—A mono-bromo-substitution product of this was obtained in almost theoretical yield; the *bromo-*o*-carbethoxybenzenediazohydroxylamino-*p*-toluene* obtained is of a pale yellow colour, melts at 148°, and crystallises in stellate aggregates of thin, sharply-pointed needles. It is very sparingly soluble in light petroleum, alcohol, or glacial acetic acid, but very readily so in benzene or chloroform, and its reactions are similar to those of the parent substance:

0·1499 gave 0·2780 CO_2 and 0·0642 H_2O. C = 50·56; H = 4·76.
0·1285 „ 12·8 c.c. N_2 at 20° and 768 mm. N = 11·52.
0·1404 „ 0·0699 AgBr. Br = 21·18.
$C_{16}H_{16}O_3N_3Br$ requires C = 50·80; H = 4·21; N = 11·11; Br = 21·16 per cent.

The aqueous extract of the reaction mixture was found to contain the merest trace of a diazonium compound.

Some experiments were also carried out on the action of bromine on the same compound in glacial acetic acid solution, when it was found that its behaviour was absolutely identical to that in chloroform.

Bromine therefore acts on this compound solely as a substituting agent, the presence of a carbethoxy-group in the ortho-position with respect to the diazohydroxylamino-grouping apparently serving as a protection against the decomposing action of the halogen.

(*b*) m-*Carbethoxybenzenediazohydroxylamino*-p-*toluene.*—In this case no trace whatever of a bromine substituted compound could be isolated. The chloroform solution, after extraction with water, left a large quantity of a dark-coloured oil, almost entirely volatile and consisting of impure *p*-nitrosotoluene.

From the aqueous extract, by the action of alkaline β-naphthol, a dark red azo-dye (m-*carbethoxybenzeneazo-β-naphthol*), melting at 105°, was obtained:

0·1452 gave 11·00 c.c. N_2 at 19° and 745 mm. N = 8·56.
$C_{19}H_{16}O_3N_2$ requires N = 8·75 per cent.

The action of bromine in glacial acetic acid was identical with that given above, so that in both solvents its action was solely one of decomposition.

(*c*) p-*Carbethoxybenzenediazohydroxylamino*-p-*toluene.*—The chloroform solution on evaporation yielded an oily, semi-liquid residue, which consisted chiefly of *p*-nitrosotoluene. On extraction with light petroleum, however, an insoluble residue was obtained, too small in amount to be submitted to analysis, but which was proved to contain bromine. The aqueous extract of the chloroform, on coupling with β-naphthol, yielded a dye, which was free from bromine. Hence bromine seems to exert almost solely a decomposing influence, substitution taking place only to a very slight extent.

Action of Bromine in Chloroform Solution on the Three Mononitrobenzenediazohydroxylamino-p-*toluenes.*

In the case of the ortho-isomeride at the ordinary temperature, no action whatever took place, whilst at higher temperatures both decomposition and substitution were effected.

The meta-isomeride suffered only decomposition, little, if any, substitution taking place, whilst identical behaviour was observed in the case of the para-isomeride.

At low temperatures, namely, at 10—15°, the ortho-isomeride remains absolutely unattacked after keeping for weeks, whilst the other two are only very slowly decomposed, thus demonstrating the protective action of the nitro-group in general and its greater protective action when in the ortho-position.

Action of Bromine in Chloroform Solution on the Three Monobromobenzenediazohydroxylamino-p-*toluenes.*

In the case of the ortho-isomeride, the action was both of a decomposing and of a substituting nature. The chief action in the case of the meta-isomeride was one of decomposition, and in the case of the para-compound almost exclusively one of substitution, the reaction therefore in general furnishing little or no criterion of the effect of the bromine atom in its three possible positions.

In conclusion, the authors desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

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CXXVII.—*Isolation and Synthesis of* p-*Hydroxyphenylethylamine, an Active Principle of Ergot soluble in Water.*

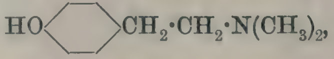
By George Barger.

In a paper on the alkaloids of ergot, F. H. Carr and the author (Trans., 1907, **91**, 337) described the amorphous alkaloid ergotoxine, to which many of the characteristic physiological effects of ergot are due. This alkaloid is, however, only present in small quantities in most specimens of the pharmacopœial preparations of ergot, and, in discussing the latter, H. H. Dale and the author (*Biochem. J.*, 1907, **2**, 286) postulated the presence of a second active principle soluble in water. Attempts to isolate this hypothetical principle were for a long time unsuccessful. Vahlen (*Arch. exper. Path. Pharm.*, 1906, **55**, 131) seems also to have been aware of the existence of such a principle, but his so-called "clavin" has been shown to be an inert mixture of amino-acids, in which leucine predominates (Barger and Dale, *Biochem. J.*, 1907, **2**, 288).

The physiological properties of *p*-hydroxyphenylethylamine, recently isolated from putrid meat by Barger and Walpole (*J. Physiol.*, 1909, **38**, 343), suggested that this base might be the above-mentioned active principle of aqueous ergot-extracts. It has indeed been possible to prove that *p*-hydroxyphenylethylamine occurs in such extracts, and that the presence of this base accounts in a satisfactory manner for such of the activity as is not due to small quantities of ergotoxine (see Barger and Dale, *Proc. physiol. Soc.*, May 15th, 1909; the physiological experiments have been performed by Dr. H. H. Dale). The method of isolation, described below, was based on the process employed in the case of putrid meat, but required further elaboration on account of the large amount of resinous constituents of ergot which are soluble in water.

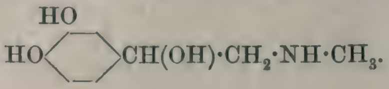
p-Hydroxyphenylethylamine has figured several times in chemical literature. It was first prepared in small quantities by Schmitt and Nasse (*Annalen*, 1865, **133**, 214), who obtained it by heating tyrosine. Subsequently it was isolated by Emerson (*Beitr. chem. Physiol. Path.*, 1902, **1**, 501) from autolysed pancreas, and by Langstein (*ibid.*, 1902, **1**, 507) in prolonged peptic digestion of egg-albumin. Gautier (*Bull. Soc. chim.*, 1906, [iii], **35**, 1195) isolated the base, together with a lower and a higher homologue, from the mother liquors obtained in the putrefaction of cod-livers. He suggested for these bases the general name "tyrosamine," since they may be considered as being derived from tyrosine and its homologues by loss of carbon dioxide. That *p*-hydroxyphenylethylamine is indeed one of the products of the action of bacteria on tyrosine was shown by Barger and Walpole (*loc. cit.*), and their recognition of its physiological action enabled Rosenheim (*J. Physiol.*, 1909, **38**, 337) to trace the substance in placental extracts, the action of which on blood pressure and uterus was first observed by Dixon and Taylor (*Brit. Med. Journ.*, 1907, ii, 1150). Rosenheim also showed that such extracts are only active if the placenta has undergone a certain amount of putrefaction. Similarly, Van Slyke and Hart (*Amer. Chem. J.*, 1903, **30**, 8) found *p*-hydroxyphenylethylamine in Cheddar cheese, but not in cheese prepared under sterile conditions. Quite recently the base was also isolated from Emmenthaler cheese by Winterstein and Künz (*Zeitsch. physiol. Chem.*, 1909, **59**, 138).

In all the above investigations, *p*-hydroxyphenylethylamine was only obtained in small quantities (generally as the dibenzoyl derivative). Even the method of preparation by the destructive distillation of tyrosine yields only small quantities. After the powerful and interesting physiological action of the substance became known, and after the substance had been recognised as the chief active principle of aqueous extracts of ergot, it became desirable to have a more convenient method of preparation, and this was found in the reduction of *p*-hydroxyphenylacetonitrile. The latter substance had already been prepared by Pschorr, Wolfes, and Buckow (*Ber.*, 1900, **33**, 171), and readily yielded the desired amine on reduction with sodium and alcohol. It thus became possible to study the properties of the substance a little more closely, and particularly to investigate its behaviour towards methylating agents. Since the alkaloid hordenine, obtained by Léger (*Compt. rend.*, 1906, **142**, 108) from malt germs, is regarded as having the structure



its synthesis, by methylation of *p*-hydroxyphenylethylamine, was attempted. By the action of methyl iodide on this base, a quaternary iodide is readily obtainable, which proved to be identical with hordenine methiodide. It is hoped that an account of these experiments, which are as yet incomplete, may be given later.

Attention may also be drawn to the somewhat close chemical and physiological relationship between the active principle of ergot under discussion and the active principle of the adrenal gland,



EXPERIMENTAL.

Isolation of p-*Hydroxyphenylethylamine from Ergot.*

Preliminary experiments had shown that the active principle in question could not be removed to any appreciable extent from aqueous extracts by extraction with ether, chloroform, or ethyl acetate. Nor could the substance be obtained by precipitation; it was, indeed, carried down to a large extent whenever a bulky precipitate was formed, as, for instance, by basic lead acetate, but it could not be recovered from these precipitates. In amyl alcohol, a solvent was, however, found which extracted the active principle from an aqueous extract, rendered alkaline by sodium carbonate, but not from one containing a sufficient quantity of sodium hydroxide or hydrochloric acid. The active substance therefore behaved like a phenolic amine. In the case of putrid meat, the purification, suggested by these properties, was sufficient to allow of the crystalline dibenzoyl derivative being obtained at once, but in the case of ergot this was not so by any means. A certain portion of the large quantity of inert matter, which still accompanied the active principle after the use of amyl alcohol, was removed by precipitation in alcoholic solution by mercuric chloride. Its final isolation, however, only became possible by utilising the (very slight) solubility of the substance in ether, which solubility had originally been overlooked. Eventually the following process was employed:

The aqueous extract from 1·5 kilos. of ergot was concentrated to 375 c.c. in a vacuum on the water-bath; it was then rendered alkaline with sodium carbonate and extracted ten times with 150 c.c. of amyl alcohol (a very tedious process on account of the formation of emulsions). The amyl alcohol extract was evaporated to 200 c.c., and extracted ten times with 30 c.c. of 1 per cent. sodium hydroxide. The sodium hydroxide was neutralised with hydrochloric acid and evaporated to dryness, and the residue was extracted with absolute alcohol, which left sodium chloride behind. The alcoholic filtrate, measuring 250 c.c., was precipitated with a saturated alcoholic solution of mercuric chloride until no further immediate precipitate occurred (about 10 c.c. were required). After filtration by the aid of the pump, the filtrate was concentrated; the remainder of the alcohol was removed by distillation in a current of steam, so that the solution was never evaporated to dryness. A precipitate, insoluble in water, was formed, and was collected; the excess of mercury was then removed by hydrogen sulphide, and the solution was concentrated to 30 c.c.

This solution, which was still strongly pigmented, was very active physiologically, 0·5 c.c. producing a large rise of blood-pressure. At each step in the purification, it was shown by physiological experiment that the loss of activity was only of such an order as the manipulations necessarily entailed. In the same way it was shown that the active substance could be removed from solution as an insoluble benzoyl derivative, and recovered by hydrolysis, but it was impossible to crystallise the benzoyl derivative, or to separate it from the complex mixture of other benzoyl derivatives. The final purification was made possible by the observation that the active principle is very slightly soluble in ether.

To the above-mentioned concentrated solution sufficient sodium hydroxide was added to make it semi-normal; the solution was then extracted ten times with half its volume of ether. This ethereal extract possessed no physiological activity. After neutralising the aqueous solution and rendering it slightly alkaline with sodium carbonate, it was again extracted ten times with half its volume of ether. On evaporation the ether left behind 0·1 gram of a dark brown, syrupy residue, which gave an intense Millon reaction, and was very active physiologically. The aqueous solution was again extracted ten times with ether, and the ethereal extract was found to possess about one-quarter of the activity of the first extract, showing that presumably nearly all, but not all, the active substance had been removed; in accordance with this the aqueous solution was now found to possess a very slight activity, much less than that of the second extract. The conclusion therefore seems justified that the whole of the active substance is (very slightly) soluble in ether.

The first ethereal extract containing the bulk of the active substance was dissolved in 3 c.c. of 10 per cent. sodium hydroxide, and benzoylated by the Schotten-Baumann method. The dark brown benzoyl derivative was boiled in alcoholic solution with animal charcoal, and separated as an amorphous, pigmented solid. This was redissolved in hot alcohol, and then separated overnight in large, almost white, sphæro-crystals, which were collected and washed with alcohol. These crystals melted at 167°. On mixing with an equal weight of synthetic dibenzoyl-*p*-hydroxyphenylethylamine (m. p. 170°), the melting point was 168·5°.

The amount of the crystalline benzoyl derivative thus obtained was too small to admit of analysis. 4·5 Milligrams were hydrolysed by boiling with 20 per cent. hydrochloric acid for twelve hours; after removal of the hydrochloric and benzoic acids, the solution gave an intense coloration with Millon's reagent, and was found to have a powerful physiological effect, almost as large as that of pure synthetic *p*-hydroxyphenylethylamine.

The slight difference in effect was doubtless due to a small portion of the benzoyl derivative not having been fully hydrolysed, or to decomposition during the prolonged boiling with acid.

After the active principle had thus been identified, 0·12 gram of synthetic *p*-hydroxyphenylethylamine was added to the inactive ergot solution, and the extraction with ether was repeated exactly as before. In the first ten extractions, 0·08 gram was now removed, and in the second ten extractions 0·02 gram, thus showing a close agreement in the partition between ether and water to that observed before by physiological means.

It is, indeed, possible, by using a sufficient quantity of ether, to show that a crude aqueous ergot extract contains a phenolic base giving the Millon reaction, but as the amount present is wholly insignificant compared with that of the inert substances accompanying it, this method would scarcely be suitable for the identification of the substance. It will be clear from the above that it is very difficult to form an estimate of the amount of *p*-hydroxyphenylethylamine in ergot by chemical means, but on physiological grounds this amount would appear to be of the order of 0·1—0·01 per cent.

Synthesis of p-*Hydroxyphenylethylamine from* p-*Hydroxyphenylacetonitrile.*

The preparation of *p*-hydroxyphenylacetonitrile from phenylacetonitrile proceeded in close agreement with the description given by Pschorr, Wolfes, and Buckow (*loc. cit.*), except that the yield on diazotisation fell somewhat short of that given by these authors, and amounted at most to 60 per cent. The intermediate products were used in their crude condition.

For the reduction, 5 grams of *p*-hydroxyphenylacetonitrile are dissolved in a small quantity of absolute ethyl alcohol, and 7—10 grams of sodium (2—3 times the theoretical quantity) are added in small pieces. The solution is kept boiling and as concentrated as possible; when sodium ethoxide separates out, more alcohol is added to dissolve it. When all the sodium has dissolved, the solution is neutralised with hydrochloric acid and evaporated to dryness. The residue, consisting mostly of sodium chloride, is extracted with absolute alcohol, and from this alcoholic solution *p*-hydroxyphenylethylamine hydrochloride can be precipitated with ether. It is, however, preferable to purify the free base. For this purpose, sodium carbonate is added to the alcoholic solution of the hydrochloride, and the solution is evaporated to dryness on the water-bath under diminished pressure; the residue may be further dried by evaporation with absolute alcohol, and is then extracted with boiling xylene until no more of the base crystallises from the filtered extracts on cooling. It is not easy to obtain the base perfectly white by recrystallisation, but this may be readily done by distillation, the boiling point being 161—163°/2 mm. and 175—181°/8 mm. For this a suitably shaped receiver is necessary, on account of the high melting point of the substance.

When crystallised from alcohol, *p*-hydroxyphenylethylamine forms hexagonal leaflets, m. p. 161°. It is soluble in about 10 parts of boiling ethyl alcohol, somewhat less in boiling water, very much less in boiling xylene, and hardly soluble in cold xylene. Xylene is a convenient solvent for recrystallisation, as it does not dissolve the resinous impurities. According to Gautier, the base is soluble in 95 parts of water at 15°. According to Schmitt and Nasse, *p*-hydroxyphenylethylamine is easily decomposed, but this the author is unable to confirm. The base gives Millon's and Mörner's reactions for tyrosine. When benzoylated in 10 per cent. sodium hydroxide with excess of benzoyl chloride, the dibenzoyl derivative, m. p. 170°, previously prepared by Emerson, is obtained. With one molecular equivalent of benzoyl chloride a certain amount of the N-*monobenzoyl* derivative, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot C_6H_5$, is formed, which crystallises from alcohol in hexagonal plates, melting at 162°, and is somewhat more soluble than the dibenzoyl derivative:

0·1300 gave 6·5 c.c. N_2 (moist) at 15° and 750 mm. N = 5·8.

$C_{15}H_{14}O_2N$ requires N = 5·8 per cent.

When picric acid is added to a hot aqueous solution of *p*-hydroxyphenylethylamine, a *picrate* melting at 200° slowly crystallises in short prisms.

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CXXVIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XV. Mixed Solvents.*

By Thomas Stewart Patterson and Harvey Hugh Montgomerie.

The variation of the rotation of an active substance under the simultaneous action of two indifferent solvents has already been the subject of several investigations by Oudemans (*Annalen*, 1873, **166**, 71; 1876, **182**, 47), Hesse (*Annalen*, 1875, **176**, 219), and Rimbach (*Zeitsch. physikal. Chem.*, 1892, **9**, 698). The results of these researches are summarised in Landolt's "*Das optische Drehungs-*

vermögen," 2te Auflage, p. 211; therefore we need only say here, regarding the experiments of Oudemans and Hesse, that cases were observed in which certain alkaloids showed a higher rotation in a mixture of two solvents at a given concentration than in either solvent separately, a phenomenon which seems to deserve some further investigation.

Rimbach's accurate and very complete research dealt with the rotation of camphor in benzene, in ethyl acetate, and in mixtures of these solvents; of turpentine in acetic acid and alcohol, and of dextrose in aqueous solutions of magnesium chloride and in aqueous solutions of calcium chloride. For camphor in ethyl acetate and benzene, and for turpentine in alcohol and acetic acid, he shows that the rotation of the active substance in the mixed solvent may be calculated approximately by a simple mixture-formula:

$$[\alpha] = [\alpha]_1 P_1 + [\alpha]_2 P_2,$$

where P_1 and P_2 are the quantities of the components contained in unit weight of the mixed solvent, $[\alpha]$ is the specific rotation of the mixture, $[\alpha]_1$ and $[\alpha]_2$ the specific rotations of the active substances in the respective solvents separately. There was, however, a slight but distinct difference in each case, which could not be accounted for by making allowance, in calculating the specific rotation of the solution, for the slight change of density on mixing. Rimbach found, further, that magnesium chloride exerted, practically speaking, no effect on the rotation of dextrose, whereas calcium chloride had a very powerful influence.

In undertaking some further work on this subject, we were actuated by the desire to throw some light on the cause of rotation-change due to solution in a single solvent, especially perhaps in regard to the possibility of the occurrence of chemical combination between solute and solvent, and we also thought that, in at least two respects, an improvement could be effected on Rimbach's choice of material. It is clearly desirable that the solvents used should have effects on the rotation of the active substance as divergent as possible, and also that the densities of the solvents should lie considerably apart; in short, that all differences should be emphasised to the maximum extent. From Rimbach's data, a $c = 20$ solution of camphor in benzene has $[\alpha]_D^{20}$ +43·3°, whilst at the same concentration it has in ethyl acetate $[\alpha]_D^{20}$ +51·9°. There is thus only a difference of 8·6° in the rotations, whilst the maximum difference which it is possible to consider is one of less than 12°; also, the specific gravities of the solvents lie very close together. For turpentine in acetic acid and in alcohol there is only a difference of less than 2° in rotation, but a somewhat greater difference than in the former case, in regard to the density of the solvents.

We chose as active substance ethyl tartrate, and as solvents, nitrobenzene and ethylene bromide. In nitrobenzene at infinite dilution ethyl tartrate has $[\alpha]_D^{20}$ +41° (Trans., 1908, **93**, 1837), and in ethylene bromide, $[\alpha]_D^{20}$ −19°, so that the effect of these two solvents is very different indeed. We were then enabled to work with fairly concentrated solutions (about $c = 24$), which, of course, renders the rotation data the more accurate. At $c = 23·938$ in nitrobenzene, ethyl tartrate has $[\alpha]_D^{20}$ +25·9°, and at $c = 23·832$ in ethylene bromide, $[\alpha]_D^{20}$ −10·72°, a difference of 36·62°, or about four times as great as in Rimbach's experiments. The density also of ethylene bromide ($d_4^{20} = 2·18141$) is nearly twice as great as that of nitrobenzene ($d_4^{20} = 1·20346$), so that solutions of equal concentration (c) are very different in weight.

It is somewhat easier, experimentally, to make up solutions with a mixed solvent to a certain definite concentration (c = grams per 100 c.c.) than to a definite percentage composition (p = grams per 100 grams solution), so in our first series of experiments we used always the same quantity (10 c.c.) of ethyl tartrate in 50 c.c. of solution, varying the relative proportions of nitrobenzene and ethylene bromide.

In preparing all the solutions care was taken to mix the liquids thoroughly before making up to the mark, to ensure that any change of volume due to mixing should be practically complete before the final adjustment was made. The concentrations quoted, however, do not depend on the graduation of the flask, but are calculated from the weight of the solution and its density. The results of our first series of experiments are given in table I.

TABLE I.

Ethyl Tartrate in Nitrobenzene, in Ethylene Bromide, and in Mixtures of these Solvents.

(Ethyl tartrate, α_D^{20} (100 mm.) + 9·372°, d_4^{20} = 1·20539; nitrobenzene, d_4^{20} = 1·20346; ethylene bromide, d_4^{2} = 2·18141.)

Number of solution.	Composition of solvent. Grams of nitrobenzene in 100 grams of mixed solvent.	c.	p.	d_4^{20}.	$\alpha_D^{20°}$ (200 mm.).	$[\alpha]_D^{20°}$.
1 ……	100·000	23·938	19·925	1·20144	+12·40°	+25·9°
2 ……	61·915	23·88	17·105	1·39611	7·62	15·95
3 ……	35·627	23·83	15·022	1·58642	3·34	7·01
4 ……	35·034	23·75	14·928	1·59099	3·225	6·80
5 ……	15·547	23·84	13·391	1·78028	−0·81	−1·70
6 ……	0·000	23·832	12·061	1·97599	−5·11	−10·72

When from the two extreme values the rotations are calculated for the intermediate solutions on the assumption that the effect of the nitrobenzene or of the ethylene bromide should be proportional to its volume in the mixed solvent, the following data are obtained.

TABLE II.

Number of solution.	Composition of solvent. Parts by volume of nitrobenzene per 100 parts by volume of mixed solvent.	$[\alpha]_D^{20^\circ}$. Observed.	$[\alpha]_D^{20^\circ}$. Calculated.	$[\alpha]_D^{20^\circ}$. Δ.	Expansion per 100 c.c. c.c.
1	100·00	+25·9°	—	—	0·200
2	74·65	15·95	16·61°	−0·66°	0·438
3	49·98	7·01	7·58	−0·57	0·572
4	49·42	6·80	7·38	−0·58	0·564
5	25·01	−1·70	−1·56	−0·14	0·588
6	0·00	−10·72	—	—	0·570

The agreement between the calculated and observed values is thus fair, but differences, which cannot be neglected, certainly occur—differences of just the same order of magnitude as those observed by Rimbach. The calculated is always higher than the actual value, and in the first three cases certainly, but probably in all, the difference is much above the experimental error. That the experimental error is not great may be judged by comparison of the data for solutions 3 and 4, which were made up purposely of an almost identical concentration. It will be seen that the differences between the calculated and observed values in these two cases are, as they should be, practically identical.

As in the case of the differences observed by Rimbach, these deviations from the calculated values cannot be explained by the slight density change on mixing. In the first place this change is in the wrong direction. The observed rotation is less than the calculated value, and to bring about this result, the density of the mixed liquid would require to be greater than that calculated from the separate values; the actual behaviour is just the opposite of this. Secondly, the change in density, even if it were in the proper sense, would require to be ten times greater than it is to annul numerically the departure of the rotation from the calculated value.

This departure from the calculated rotation values may perhaps be accounted for as follows. Each pair of the three liquids used mix with expansion. For ethyl tartrate in nitrobenzene, and ethyl tartrate in ethylene bromide, this can be shown by means of the data already given, whilst for mixtures of ethylene bromide and nitrobenzene we obtained the following numbers:

Composition of mixture in grams.				Expansion per 100 c.c.
Nitrobenzene.	Ethylene bromide.	d_4^{20} (experimental).	d_4^{20} (calculated).	c.c.
23·9307	28·7086	1·58799	1·5929	0·312
31·5120	19·3252	1·44710	1·4505	0·228

The calculated density is in both cases greater than that found. In the last column is shown the expansion on mixture of such quantities, taken in the proportions quoted, as, separately, occupy 100 c.c.

Now it has been shown by one of us that, at least for ethyl tartrate in a variety of solvents, there appears to be a relationship between the volumes of the dissolved ester and its rotation in a given solvent. Roughly speaking, it is to be expected that if ethyl tartrate be dissolved separately in two liquids, the rotation will be greater in the solution having the smaller volume. For instance, as is shown in table II, the expansion (0·2 c.c.) on mixing 19·86 c.c. of ethyl tartrate with 79·94 c.c. of nitrobenzene is only about one-third of the expansion (0·57 c.c.) which occurs on mixing 19·77 c.c. of ethyl tartrate with 79·66 c.c. of ethylene bromide. In harmony with this, the rotation in the nitrobenzene solution is much higher than in the ethylene bromide solution.* Now since the expansion is greater for the three component than for the two component mixtures (see the last column of table II), the internal forces in the former may be less than a simple mixture law would lead us to expect, for which reason the rotation has a lower than the calculated value.

As an alternative explanation it might be supposed that the ethylene bromide has a slightly superior "attraction" for the ethyl tartrate, so that its influence preponderates in the mixture. By "attraction" we mean that property of a liquid, or a property similar to that in consequence of which it is capable of holding another substance in solution, a mutual affinity which it does not seem necessary to regard as identical with chemical combination. This attraction would presumably be composed of two factors, one due to the solvent and one to the solute, and a relative measurement of it is probably obtained by distributing a given solute between two immiscible solvents.

The idea that the influence of a solvent on the rotation of an active compound may be a measure of this affinity is of interest, but only very little experimental work exists by which it can be tested. Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 586) has examined the distribution of ethyl tartrate between ethylene bromide and water and finds it to be, in dilute solution, about 1 : 6. The attraction of water for ethyl tartrate is thus much greater than that of ethylene bromide, and the rotation in the former is, of course, much greater than in the latter solvent. Winther's experiments also show that the attraction of formamide for ethyl tartrate is very much greater than that of ethylene bromide—but this case seems to be peculiar—whilst the distribution ratio of ethyl tartrate in benzene : water is about 1 : 5, which is again in qualitative agreement with the rotation data. From these facts, however, it would hardly seem probable that ethylene bromide should have a stronger attraction for ethyl tartrate than has nitrobenzene, but the matter is worth some further investigation.

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* It is true, however, that this assumption of a relationship between volume and rotation in the above instances is very distinctly open to criticism, the chief reason being that, since ethyl tartrate and nitrobenzene mix with expansion, the specific rotation of the solution ought to be less than that of the homogeneous ester instead of being, as is actually the case, much greater.

It appears then from our experiments that if two solutions of ethyl tartrate of equal volume-concentration (c),* one in nitrobenzene and one in ethylene bromide, be filled respectively into two tubes of equal length (l), the rotation, taken through these two tubes placed one behind the other, will be almost the same as the rotation observed in a tube of length $2l$, after mixing the two solutions.

As already mentioned, the two solvents we used were very different in density, and therefore in discussing the rotations of solutions in nitrobenzene and ethylene bromide it may make a great deal of difference whether comparison be instituted between solutions of equal percentage composition or of equal volume-concentration. We thought therefore that it would be of interest also to carry out a series of experiments in which the percentage composition of the solution, with reference to ethyl tartrate, was kept constant and the proportion of the two solvents varied. Our results are shown in table III. Solutions Nos. 7, 8, and 9 were made up specially for this purpose solution No. 1 is the same as appears in tables I and II.

TABLE III.

Number of solution.	Proportion of nitrobenzene in solvent.						
	Weight.	Volume.	p.	c.	d_{4}^{20}.	$\alpha_{D}^{20°}$ ($l=2$).	$[\alpha]_{D}^{20°}$.
1....	100·00	100·00	19·925	23·938	1·20144	+12·4°	+25·90°
7....	49·95	63·17	19·922	29·08	1·45966	6·69	11·50
8....	33·35	47·55	19·926	31·34	1·57267	3·8	6·06
9....	0·00	0·00	19·942	37·19	1·86496	−5·77	−7·56

TABLE IV.

Number of solution.	$[\alpha]_{D}^{20°}$.						
	Observed.	Calculated. I.	Δ.	Calculated. II.	Δ.	Calculated. III.	Δ.
1...	+25·90°	—	—	—	—	—	—
7...	11·50	+9·1°	+2·40°	+12·3°	−0·8°	+11·36°	+0·14°
8...	6·06	3·6	+2·46	6·47	−0·4	5·97	+0·09
9...	−7·56	—	—	—	—	—	—

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* Solutions presumably of equal osmotic pressure.

In table IV are shown the observed rotations along with values calculated on different assumptions. The first assumption one would naturally make is that the rotation should vary directly with the weight proportion of the constituents of the mixed solvent. This is the same thing as supposing solution No. 7, for instance, to be split up into two solutions, one of 9·951 grams of ethyl tartrate in 40 grams of nitrobenzene, and the other of 9·971 grams of ethyl tartrate in 40·078 grams of ethylene bromide. These two solutions are of the same percentage composition as the original solution, but whilst the volume of the former would be 41·58 c.c., that of the latter would only be 26·84. These two solutions may be supposed to be placed in a tube of 1 sq. cm. cross section and divided by a partition into two compartments just long enough to contain the two solutions, and it can easily be calculated from the data for solutions Nos. 1 and 9 that the superimposed observed rotations in the divided tube would amount to +18·04°, whence taking into account the density of solution No. 7, the theoretical rotation for the mixed solution, if no change occurred on mixing, would be +9·1°.

It is clear, however, from our data that if the partition in the tube were removed and the solutions allowed to mix, the observed rotation would alter from +18·04° to +22·88°, an increase of about 27 per cent. of the original value.

This is a result we had not foreseen, but it is probably to be explained as follows, and this constitutes our second method of calculation in table IV. The osmotic pressure of the two solutions just discussed would, of course, have very different values, and if we imagine the partition in the tube to be a semipermeable membrane, allowing ethyl tartrate to pass freely, but confining the solvents to their respective divisions of the tube, then the active ester would diffuse out of the ethylene bromide into the nitrobenzene until the concentrations in the two solvents were equalised.* At the same time the volume of the nitrobenzene solution would increase, whilst that of the ethylene bromide diminished, to allow for which we may suppose the partition to change its position in the tube. Neglecting small volume changes due to the fact that the volume of the mixtures is not strictly additive, the tube will now contain 43·88 c.c. of a $p=24·29$ ($c=29·23$) solution of ethyl tartrate in nitrobenzene, and 24·26 c.c. of a $p=15·04$ ($c=29·23$) † solution of ethyl tartrate in ethylene bromide. The observed rotation of the former, from data given by one of us (Trans., 1908, **93**, 1856), would be +31·28°, and of the latter, from data by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 578) and some of our own observations, it would be −6·84°, the sum being therefore +24·44° instead of the 22·88° actually determined. The specific rotation calculated in this manner would thus have the value +12·3°, which is in excess of the observed value, +11·5°, by a quantity of the same order as the differences in table II.

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* This ignores the possibility of a different degree of association of the ethyl tartrate in the two solvents. The degree of association is in fact, however, much the same in both.

† These concentrations are greater than that of the original solution (No. 7), because the sum of the separate volumes (68·14 c.c.) is less than that of the mixed solution (68·51 c.c.).

The series of observations for constant concentration and the series for constant percentage composition are thus brought into harmony, and it seems fairly clear that the influence of either of these two solvents on the rotation of ethyl tartrate may be taken as almost directly proportional to its volume, but not to its weight.

We noticed, however, by chance, that the rotation values for this series can be calculated very closely when the specific rotation of a mixture is assumed to be proportional to the mean of the percentage composition of the solvent by weight and by volume. Thus, for solution No. 7 in table III, the rotation is proportional to 56·56, the mean of 49·95 and 63·17. This gives the value 11·36° instead of the experimental 11·5°, the difference being thus very slight, whilst the agreement is even better for solution No. 8. The specific rotation, $[\alpha]$, of the mixed solution is thus given by the expression:

$$[\alpha] = \tfrac{1}{2}\left\{[\alpha]_1\frac{w_1}{w_1+w_2} + [\alpha]_2\frac{w_2}{w_1+w_2} + [\alpha]_1\frac{\dfrac{w_1}{d_1}}{\dfrac{w_1}{d_1}+\dfrac{w_2}{d_2}} + [\alpha]_2\frac{\dfrac{w_2}{d_2}}{\dfrac{w_1}{d_1}+\dfrac{w_2}{d_2}}\right\},$$

where $[\alpha]_1$ and $[\alpha]_2$ are the specific rotations of solutions of a given percentage composition in the two solvents, w_1 and w_2 the percentage weight of each solvent in the mixed solvent, d_1 and d_2 the densities of the solvents. The numbers in the seventh column of table IV were calculated in this way, but the physical meaning of this method of calculation is not quite clear.

It seemed also worth while to determine whether the calculated value for rotation agrees more closely with that found experimentally,

TABLE V.

Number of solution.	p.	Composition of 100 grams of solution in gram-mols.			Composition of solvent. Percentage number of molecules of nitrobenzene.	$[\alpha]_D^{20°}$.		
		Ethyl tartrate.	Nitro-benzene.	Ethylene bromide.		Obs.	Calc.	Δ.
V......	21·1	0·0729	0·5371	0·0000	100·00	+25·6°	—	—
3	15·02	0·0729	0·2461	0·2910	45·82	7·01	6·2°	+0·81°
W ...	12·95	0·0729	0·0000	0·5371	0·00	−10·3	—	—

when the influence of a solvent is regarded as proportional to the number of its molecules present in the solution. This method has recently been warmly advocated by Armstrong. Table V shows the kind of agreement that is obtained.

The rotation of solution *V* is derived from experiments by Patterson (Trans., 1908, **93**, 1856), and that of solution *W* from data recorded by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 578). It will be observed that the calculated value is in this case less than that observed. The deviation is thus in the opposite sense from, and is also somewhat greater than, that found in table II, where the composition of the solvent is taken by volume.

Heat of Mixture of Various Liquids.

It seems strange that the heat and volume changes accompanying the mixture of indifferent liquids should have attracted comparatively little attention. Work has been done on the subject by Bussy and Buignet (*Ann. Chim. Phys.*, 1865, (iv), **4**, 5), by Dupré (*Proc. Roy. Soc.*, 1872, **20**, 336), by Guthrie (*Phil. Mag.*, 1884, (v), **18**, 495), by Clarke (*Physikal. Zeitsch.*, 1905, **6**, 154), and particularly by Timoféeff, whose paper, however, is only accessible to us in abstract (*Chem. Zentr.*, 1905, ii, 429; Abstr., 1905, **86**, ii, 678). Since no generalisation has been arrived at which we could consider with reference to rotation in solution, we measured some temperature changes which occur on mixing ethyl tartrate and a number of the solvents that have been used at various times in this investigation. Ethyl tartrate (10 c.c.), contained in a test-tube provided with a stirrer, was placed in a thermostat at or near 20°. An equal quantity of solvent was placed in another test-tube in the same thermostat. The liquids,

TABLE VI.

Volume Change and Temperature Change Attending Mixture of Certain Liquids.

Mixture of	Δt.[*]	Δv[*] in c.c.	Volume of first liquid in c.c.	Volume of second liquid in c.c.	*p*.
Ethyl tartrate : water	+0·5°	−2·03	54·47	45·53	50·225[†]
,, ,, : ethylene bromide	−2·75	+0·57	19·88	80·12	12·061
,, ,, : nitrobenzene......	−1·2	+0·20	19·9	80·10	19·925
,, ,, : methyl alcohol...	+0·05	−1·52	39·63	60·37	50·00[‡]
,, ,, : benzaldehyde ...	+0·35	−0·24	32·41	67·59	35·5[‖]
,, ,, : quinoline	+9·5	−0·70	19·75	80·25	21·34[‖]
Ethylene bromide : quinoline ...	−0·5	+0·03	34·46	65·54	51·19
,, ,, : nitrobenzene.	−2·2	+0·32	39·82	60·18	54·54

[*] It is particularly to be observed that whereas the temperature changes are for equal volumes of the liquids, the volume changes are those which result on mixture of the quantities quoted in columns 4 and 5 of the table.

[†] Trans., 1904, **85**, 1154. [‡] Trans., 1901, **79**, 201. [‖] Trans., 1909, **95**, 325.

when they had attained to the same temperature, were mixed, and the change of temperature noted. The results, which of course do not indicate the quantity of heat evolved, are given in table VI, a rise being denoted by the + sign and a fall by the − sign. In the table are also given some data for the volume changes on mixing these different liquids.

Thus, 54·47 c.c. of ethyl tartrate and 45·53 c.c. of water give 97·97 c.c. of the mixture. The resulting contraction of 2·03 c.c. is entered in column 3, and the percentage composition of the solution, in terms of the first of the two liquids under consideration, is shown in the last column.

Although Bussy and Buignet, and also Timoféeff, have noticed in certain instances a different behaviour,* the volume and temperature changes recorded above are entirely in (qualitative) harmony, and the same was found by Guthrie and by Clarke for the mixtures which they examined. In each case a rise of temperature is accompanied by contraction, and a fall of temperature by expansion.

The temperature or volume changes are, however, not apparently connected with rotation in solution. Thus, water and nitrobenzene both cause a considerable rise in the rotation of ethyl tartrate, but they produce opposite temperature effects, and, on the other hand, whilst nitrobenzene causes a great increase of rotation and ethylene bromide a great depression, the temperature change is, in both cases, in the same sense. Further, whilst benzaldehyde and quinoline at about $p = 50$ produce, in ethyl tartrate, nearly the same specific rotation, the temperature effects differ greatly.

Very various opinions seem to be held as to the reason for temperature and volume changes on mixture of such liquids. The phenomenon is probably complex; true solution, whatever that may turn out to be, has perhaps always one definite effect, or it may have none, as some appear to hold, and association, dissociation, chemical combination may produce other effects, superposition of which makes investigation of the question difficult. But since one of the most important accompaniments of a spontaneous chemical combination is development of heat, it seems justifiable, where a heat development seems exceptionally great, to adopt, as a preliminary working hypothesis, the idea of combination.

Of the substances in the above table, that which mixes with ethyl tartrate with the greatest elevation of temperature is quinoline, and quinoline had already attracted our attention as a solvent for ethyl tartrate, it having shown itself to be peculiar in regard to its influence on the rotation of the ester (Trans., 1909, **95**, 323), and this might possibly be due to combination of solvent with solute.

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* The behaviour of twenty-four pairs of liquids is shown in a table on p. 257 of Sydney Young's *Stoichiometry*. In six cases, the heat and volume changes are not in harmony.

Cryoscopic Experiments with Two Solutes Present Together.

Thinking that cryoscopic molecular-weight determinations might be of interest in this connexion, we carried out the following experiments. Nitrobenzene in regard to its influence on the rotation of ethyl tartrate may be said to be normal,* whence we should be inclined to postulate the absence of chemical combination between the two substances, more especially since the heat of mixture is negative. The same remarks apply to a solution of ethyl tartrate in ethylene bromide. We therefore determined, firstly, the depression of the freezing point of ethylene bromide produced by addition of ethyl tartrate; secondly, the depression of the freezing point of ethylene bromide produced by addition of nitrobenzene, and, thirdly, the depression due to an equimolecular mixture of ethyl tartrate and nitrobenzene. If in the last case no combination occurs between the two solutes, the depression of freezing point might be expected to be practically the sum of the separate depressions. The results were as follows:

TABLE VII.

Ethyl Tartrate (M.W. = 206) *in Ethylene Bromide* (K = 118).

Weight of solute.	Weight of solvent.	Grams solute per 100 grams solvent.	Centigram-molecules solute per 100 grams solvent.	Δ.	M.W.
0·3603	45·55	0·791	0·38	0·41°	228
0·6392	45·55	1·4033	0·68	0·69	240
1·2059	41·127	2·932	1·42	1·323	261
2·4018	41·127	5·839	2·83	2·252	306
3·8518	41·127	9·365	4·55	3·125	354
Nitrobenzene (M.W. = 123) *in Ethylene Bromide.*					
1·0137	39·6705	2·555	2·08	2·297°	131
1·7640	39·6705	4·447	3·61	3·762	139
2·2441	39·6705	5·657	4·60	4·667	143
1·2448	34·4451	3·614	2·93	3·190	134
1 6119	34·4451	4·680	3·80	4·025	137
2·0291	34·4451	5·891	4·79	4·942	141

* These results agree closely with data given by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 584).

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* Since the rotation of the dissolved ester appears to vary, on change of temperature, according to the same law as holds for many other solvents (Trans., 1909, **95**, 323).

Mixture of Ethyl Tartrate (1 *mol*.) *and Nitrobenzene* (1 *mol.*) *in Ethylene Bromide.*

Weight of solute.	Weight of solvent.	Centigram-molecules of each constituent per 100 grams solvent.	Δ.		
			Observed.	Calculated.	Difference.
0·5508	35·7865	0·4678	1·083°	1·02°	+0·06°
1·0966	35·7865	0·9314	2·020	1·97	+0·05
1·7639	35·7865	1·4982	2·948	3·15	−0·20
2·2950	35·7865	1·9492	3·665	3·85	−0·19
3·0266	35·7865	2·5706	4·563	4·89	−0·33
—	—	3·12 *	5·22 *	5·67	−0·45

* By extrapolation.

It will be observed from these results that the apparent association of ethyl tartrate in ethylene bromide is considerable. The molecular weight of the ester at the highest concentration ($p = 8{\cdot}56$) is almost twice the theoretical. On the other hand, nitrobenzene shows but little association in ethylene bromide.

When the two substances are dissolved together in ethylene bromide, they seem to interfere with one another only to a slight extent, since the observed depression is nearly that which was to be expected from the separate depressions.

We next carried out similar experiments, first with quinoline and then with a mixture of quinoline and ethyl tartrate in ethylene bromide, and obtained the results shown in table VIII.

TABLE VIII.

Quinoline (M.W. = 129) *in Ethylene Bromide.*

Weight of solute.	Weight of solvent.	Grams solute per 100 grams solvent.	Centigram-molecules solute per 100 grams solvent.	Δ.	M.W.
0·7746	45·79	1·692	1·3116	1·490°	134
1·4288	45·79	3·120	2·4185	2·697	136
1·8877	45·79	4·122	3·195	3·587	136
2·3143	45·79	5·054	3·918	4·327	138
2·6057	45·79	5·690	4·411	4·80	140

Mixture of Ethyl Tartrate (1 *mol.*) *and Quinoline* (1 *mol.*) *in Ethylene Bromide*

Weight of solute.	Weight of solvent.	Centigram-molecules of each constituent per 100 grams solvent.	Δ.		
			Observed.	Calculated.	Difference
0·5274	39·081	0·40	0·853°	0·895°	0·04°
1·2220	39·081	0·93	1·780	1·97	0·19
1·9607	39·081	1·50	2·615	3·03	0·42
2·6812	39·081	2·05	3·330	4·01	0·68
4·08	39·081	3·12	4·563	5·81	1·25

Quinoline and nitrobenzene thus behave very similarly in ethylene bromide solution, quinoline showing, however, slightly less apparent association than nitrobenzene.

From the second set of figures it appears that ethyl tartrate and quinoline interfere much more with each other in ethylene bromide solution than do ethyl tartrate and nitrobenzene, since the observed depression is very distinctly less than the sum of the separate depressions. For the latter pair at a concentration of 3·12 cgm.-mols. per 100 grams of solvent, the sum of the separate depressions should be 5·67°, whilst the experiments give (on extrapolation) 5·22°, a difference of only 0·45°, whilst in the case of ethyl tartrate and quinoline the corresponding difference is 1·247°.

Although we are not prepared to admit that numbers obtained even in only moderately concentrated solution by the cryoscopic method really represent average molecular weights,* we think the above facts may be regarded at least as presumptive evidence in favour of combination between ethyl tartrate and quinoline, and we may also point out that if, in the last solution in the tables, the quinoline were to be replaced by ethyl tartrate molecules, making the concentration of the tartrate 6·24 cgm.-mols. per 100 grams of ethylene bromide, the observed depression would then be 3·65° instead of $2 \times 2{\cdot}38 = 4{\cdot}76°$ (that is, twice the depression observed in a solution of 3·12 cgm.-mols. per 100 grams of ethylene bromide †). The difference, 1·11°, is thus less than that found for the quinoline-ethyl tartrate solution, so that the apparent tendency of the quinoline molecules to combine with ethyl tartrate molecules is greater than the tendency of ethyl tartrate molecules to combine amongst themselves.

The Rotation of Ethyl Tartrate in Mixtures of Quinoline and Ethylene Bromide.

Since the solvent influence on rotation, the temperature change on mixing, and these cryoscopic experiments all seemed to indicate a difference either of degree or kind in the behaviour of quinoline as compared with a number of other solvents, we thought it would also be of interest to examine the solvent effect of mixtures of quinoline and ethylene bromide on the rotation of ethyl tartrate in the same manner as already described for mixtures of nitrobenzene and ethylene bromide. The concentration of the ethyl tartrate was kept constant and at the same value as before. The quinoline had d_4^{20} 1·09392, and the ethylene bromide (a fresh sample), d_4^{20} 2·18157.

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* The formula being valid only for infinitely dilute solution. We have no theoretically sound way of modifying the formula to suit concentrated solutions.

† By interpolation from data given in the first part of table VII.

TABLE IX.

No. of solution.	Composition of solvent. Quinoline. Per 100 grams mixed solvent.	Per 100 c.c. mixed solvent.	c.	p.	d_4^{20}.	$\alpha_D^{20°}$ (200 mm.).	$[\alpha]_D^{20°}$ Obs.	Calc.	Δ.	Expansion per 100 c.c. in c.c.
10	100·0	100·0	23·9604	21·3389	1·12396	+12·62°	+26·32°	—	—	−0·70
11	42·3	58·96	23·9604	16·177	—	+ 7·02	+14·65	+11·1°	+3·55°	—
12	32·95	49·5	23·9606	15·3182	1·56068	+ 5·25	+10·98	+ 7·9	+3·08	− 0·26
6	0·0	0·0	23·832	12·061	1·97599	− 5·11	− 10·72	—	—	+0·57

It will be seen from these data that the value of the rotation in the mixed solvent (+ 14·65°) is much higher than that calculated (+ 11·1°) on the assumption that the effect of the solvent is proportional to its volume. There is thus a distinct contrast between the quinoline-ethylene bromide and the nitrobenzene-ethylene bromide mixtures. The numerical difference between the calculated and observed values is about five times as great in the former case as in the latter, and it is in the opposite sense. The fact that the observed value is greater than the calculated would seem to indicate that the quinoline in the mixture has the preponderating influence, which is what might be expected from the cryoscopic and other experiments referred to above. It may also be remarked that the volume change (− 0·26 c.c.) in the three component system (solution 12) is a greater contraction than would be expected (− 0·055 c.c.) from the volume changes in solutions 10 and 6. This is also in agreement with the high rotation and in harmony with the relationship between volume change and rotation change which was referred to in connexion with the nitrobenzene-ethylene bromide mixtures.

Starting from the assumption that the rotation ought to be calculated as proportional to the molecular percentages of the solvents present, we find for the quinoline-ethylene bromide solutions the figures of table X, in which the data for solutions *X* and *Y* are

TABLE X.

Number of solution.	p.	Composition of 100 grams of solution in gram-molecules. Ethyl tartrate.	Quinoline.	Ethylene bromide.	Composition of solvent. Percentage number of molecules of quinoline.	$[\alpha]_D^{20°}$. Obs.	Calc.	Δ.
X ...	18·6	0·07436	0·5182	0·0000	100·00	+ 26·00°	—	—
12 ...	15·3182	0·07436	0·2162	0·3020	41·74	10·98	+ 5·0°	+ 5·98°
Y ...	13·589	0·07436	0·0000	0·5182	0·00	− 9·95	—	—

calculated from results recorded in Trans., 1909, **95**, 326, and *Zeitsch. physikal. Chem.*, 1907, **60**, 578, respectively. By this method the difference between the calculated and observed rotations is thus much greater than when the influence of each solvent is taken as proportional to its volume, but that of course does not decide which process, if either, is correct.

In conclusion we may summarise our results as follows:

1. The influence of mixtures of nitrobenzene and ethylene bromide on the rotation of ethyl tartrate is approximately proportional to the volume composition, but not to the weight composition of the mixed solvent. From a consideration of Rimbach's data and our own, we are inclined to think that this will prove to be the normal behaviour.

2. The influence of mixtures of quinoline and ethylene bromide on the rotation of ethyl tartrate is neither proportional to the volume nor to the weight composition of the mixed solvent.

3. The depression of the freezing point of ethylene bromide produced by a mixture of ethyl tartrate and nitrobenzene is only slightly less than the sum of the depressions that would be produced by the two solutes separately. A mixture of ethyl tartrate and quinoline, on the other hand, gives a depression considerably less than that which might be expected. It would thus appear that ethyl tartrate and quinoline have at least a greater tendency to combine with each other than have ethyl tartrate and nitrobenzene.

4. Ethyl tartrate and nitrobenzene mix with absorption of heat; quinoline and ethyl tartrate mix with a very decided rise of temperature. This behaviour is also suggestive of compound formation in the latter case.

5. The peculiar influence of quinoline as a solvent on the rotation of ethyl tartrate, in regard particularly to change of rotation on heating, may perhaps also be a manifestation of compound formation.

The polarimetric measurements here recorded were carried out by means of a large Schmidt and Haensch polarimeter kindly placed at our disposal by the Carnegie Trustees for the Universities of Scotland, to whom, therefore, we beg to offer our hearty thanks.

THE UNIVERSITY,
GLASGOW.

CXXIX.—*The Action of Phosphorus Pentachloride on Benzamide.*

By Arthur Walsh Titherley and Elizabeth Worrall.

During an investigation, which is still in progress, of the behaviour of secondary amides with phosphorus pentachloride, the action of the latter on simple primary amides came incidentally under consideration. Practically the whole of our available knowledge of the behaviour of primary amides with phosphorus pentachloride arises from Wallach's extensive investigation (*Annalen*, 1877, **184**, 1), which apparently left little further to be done in this direction. The net result of his work, based chiefly on the case of ethyl oxamate (oxamethane) led him to the conclusion (i) that the carbonylic oxygen in the amido-group was first replaced by two chlorine atoms; (ii) that the resulting "dichloramide" (I) which was very unstable, readily lost hydrogen chloride (1 molecule), yielding the unstable "imide chloride" (II), and (iii) that the latter finally lost another molecule of hydrogen chloride, yielding the nitrile, thus:—

$$\cdot CO\cdot NH_2 \xrightarrow{PCl_5} \underset{(I.)}{\cdot CCl_2\cdot NH_2} \xrightarrow{-HCl} \underset{(II.)}{\cdot CCl\colon NH} \xrightarrow{-HCl} \cdot CN.$$

In the case of oxamethane, unstable derivatives of types (I) and (II) were isolated in an impure condition, but apparently, in the case of all the other amides investigated, phosphorus derivatives containing oxygen and chlorine were produced. A derivative containing phosphorus was also obtained by Wallach in the case of oxamethane, having the formula $C_4H_6O_3Cl_4NP$. In the case of benzamide, with phosphorus pentachloride in the cold, Wallach obtained a liquid which he considered to be a mixture of benzonitrile and phosphoryl chloride, but by gentle warming he obtained a liquid which, on cooling strongly, set to a crystalline mass containing phosphorus. This solid compound decomposed at once in air, and was not further investigated.

A critical survey of Wallach's results would suggest that the general action of phosphorus pentachloride on simple primary amides leads to the production of phosphorus compounds and not the simple derivatives of types I and II, and that such phosphorus compounds readily decompose on heating yielding phosphoryl chloride and the corresponding nitrile. The inconclusiveness of Wallach's results with respect to benzamide led the authors to examine its behaviour with phosphorus pentachloride more closely. The conclusions which have been arrived at are mentioned below, but after these had been reached and the work had been nearly completed, a recent paper by Steinkopf

(*Ber.*, 1908, **41**, 3571) came under the authors' notice, in which the action of phosphorus pentachloride on halogenated acetamides is described, and, to a large extent, similar conclusions have been drawn. Originally it was intended by the authors to describe their work on benzamide and dibenzamide in one paper, but as the portion referring to the latter is incomplete, it was considered advisable, since Steinkopf is at work in a similar field, to publish at once the results so far as they relate to benzamide.

When benzamide and phosphorus pentachloride react at 15°, slightly more than one molecular equivalent of hydrogen chloride is evolved, and since in no circumstances does interaction occur without formation of hydrogen chloride it is clear that the 'dichloride,' $C_6H_5 \cdot CCl_2 \cdot NH_2$ (*αα*-dichlorobenzylamine), cannot be formed except as an intermediate stage. The production of this derivative, however, as a first stage in the reaction can hardly be doubted in view of the general facts established by Wallach. In the subsequent change involving elimination of one molecule of hydrogen chloride, two things may be expected, namely, (i) the *αα*-dichlorobenzylamine may lose hydrogen chloride, yielding *α*-chlorobenzimide, or (ii) it may react with the phosphoryl chloride present, yielding a phosphorus derivative :

$$\text{I.}\quad C_6H_5 \cdot CCl_2 \cdot NH_2 \longrightarrow C_6H_5 \cdot CCl{:}NH + HCl.$$

(*α*-Chlorobenzimide.)

$$\text{II.}\quad C_6H_5 \cdot CCl_2 \cdot NH_2 + POCl_3 \longrightarrow C_6H_5 \cdot CCl_2 \cdot NH \cdot POCl_2 + HCl.$$

(*αα*-Dichlorobenzylphosphamic chloride.)

In any case the liquid obtained in the action between benzamide and phosphorus pentachloride at 15° cannot be a mixture of benzonitrile and phosphoryl chloride as Wallach supposed, since such a mixture would require the loss of two molecular equivalents of hydrogen chloride. This liquid, on treatment with water, yields benzonitrile, whilst on keeping in the cold for several hours in absence of moisture it slowly loses a molecule of hydrogen chloride, leaving a mixture which consists essentially of benzonitrile and phosphoryl chloride, and the same result is attained very rapidly by heating the liquid produced at 15° to 50°. A totally different result, however, is obtained if the action between benzamide and phosphorus pentachloride is carried out at 50°, or even at 15°, when such solvents as benzene or chloroform are present. The resulting liquid obtained under these conditions on careful treatment with water yields a mass of colourless crystals containing chlorine and phosphorus, which on investigation proved to be a benzoyl derivative of phosphamic chloride, namely, $C_6H_5 \cdot CO \cdot NH \cdot POCl_2$.

This remarkable difference in results, produced by such slight difference in conditions, led the authors to examine closely the products obtained under a large variety of conditions, and the conclusions arrived at may be stated thus :

I. In the cold without solvent the 'dichloramide,' first formed, immediately loses hydrogen chloride, yielding chiefly a mixture of α-chlorobenzimide, $C_6H_5\cdot CCl\colon NH$, and phosphoryl chloride, together with other products in small quantities (see p. 1148). The former is very unstable, and decomposes slowly at 15°, and immediately at 50°, or, on treatment with water, into benzonitrile and hydrogen chloride. On account of its instability it is impossible to isolate this α-chlorobenzimide, which, moreover, could not be separated by strong cooling or treatment with light petroleum.

II. In the cold, in presence of benzene or chloroform, the 'dichloramide' first formed immediately reacts with the phosphoryl chloride simultaneously produced, yielding αα-dichlorobenzylphosphamic chloride, $C_6H_5\cdot CCl_2\cdot NH\cdot POCl_2$, which, on heating to 50°, loses hydrogen chloride, yielding α-chlorobenzylidenephosphamic chloride :

$$C_6H_5\cdot CCl_2\cdot NH\cdot POCl_2 \longrightarrow C_6H_5\cdot CCl\colon N\cdot POCl_2 + HCl.$$

This product, moreover, results directly when benzamide and phosphorus pentachloride, without a solvent, are heated to 50°, two molecules of hydrogen chloride being evolved, but a considerable amount of benzonitrile and phosphoryl chloride is also formed. The influence of a solvent in inducing the formation of phosphorus derivatives is very striking, and by adding benzene at different stages of the action and examining the resulting product, after exposure to moist air, for benzoylphosphamic chloride, it was possible to show that the influence of the solvent in the reaction between benzamide and phosphorus pentachloride is not operative after the first molecule of hydrogen chloride has been evolved, but exerts itself in the reaction involving elimination of hydrogen chloride. The effect of a solvent, which is similar to that of heat, must be to induce the hypothetical αα-dichlorobenzylamine to react with the phosphoryl chloride with liberation of hydrogen chloride, whilst in absence of solvent at lower temperatures the αα-dichlorobenzylamine spontaneously decomposes without acting on the phosphoryl chloride, yielding α-chlorobenzimide, $C_6H_5\cdot CCl\colon NH$. There is, however, no direct proof available of the actual production of the latter compound ; treatment of the supposed mixture of this substance and phosphoryl chloride with a benzene solution of aniline at low temperatures failed to yield phenylbenzamidine, but having regard to the great instability which might be expected to characterise α-chlorobenzimide, it is likely that the aniline simply effected removal * of hydrogen chloride yielding benzonitrile

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* A similar removal of hydrogen chloride by aniline has been shown to take place with certain phosphorus derivatives (see p. 1146).

which was found. Moreover, attempts to prepare *a*-chlorobenzimide by the action of hydrogen chloride on benzonitrile at low temperatures were unsuccessful.

In regard to the two possible reactions,

$$\text{I. } C_6H_5{\cdot}CCl_2{\cdot}NH_2 \longrightarrow C_6H_5{\cdot}CCl{:}NH + HCl.$$

$$\text{II. } C_6H_5{\cdot}CCl_2{\cdot}NH_2 + POCl_3 \longrightarrow C_6H_5{\cdot}CCl_2{\cdot}NH{\cdot}POCl_2 + HCl,$$

it would appear that whilst the velocity of (I) is not influenced by benzene and chloroform the velocity of (II) is greatly accelerated by these solvents and by rise of temperature. As already noted, Wallach (*loc. cit.*) isolated a compound similar to that formed in (II), by the action of phosphorus pentachloride on oxamethane. The product of the action in the cold was a clear liquid, evidently consisting of a mixture of phosphoryl chloride and the unstable compound,

$$CO_2Et{\cdot}CCl_2{\cdot}NH_2,$$

which was precipitated in needles by light petroleum. The mother liquor, however, on keeping, deposited crystals the composition of which corresponded with the formula $CO_2Et{\cdot}CCl_2{\cdot}NH{\cdot}POCl_2$. The most interesting feature, however, in connexion with this substance is the fact that it was only formed under the catalytic influence of a trace of moisture. As in the authors' experiments moisture was carefully excluded by means of phosphoric oxide, it is probable that benzene and chloroform behaved catalytically in a similar manner, that is, accelerating reaction (II) above, and indeed it was shown in one experiment that a relatively small quantity of chloroform gave a nearly quantitative yield of the phosphorus derivative.

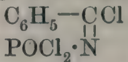
The behaviour of *a*-chlorobenzylidenephosphamic chloride with moisture is very remarkable, seeing that the two chlorine atoms attached to phosphorus escape action, whilst that attached to carbon is replaced by hydroxyl, yielding the benzoylphosphamic chloride,

$$C_6H_5{\cdot}C(OH){:}NPOCl_2 \rightleftarrows C_6H_5{\cdot}CO{\cdot}NH{\cdot}POCl_2,$$

already referred to, from which benzoylphosphamic acid,

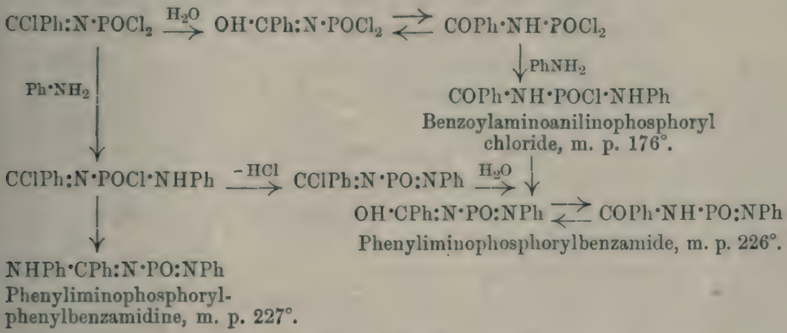
$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}PO(OH)_2.$$

may be readily obtained. This curious action is probably attributable to the steric hindrance of the phenyl group, and suggests that the trichloro-derivative has an *anti*-configuration,



$$\begin{array}{l} C_6H_5{-}CCl \\ \qquad\quad \| \\ POCl_2{\cdot}N \end{array}.$$

Both chlorobenzylidenephosphamic chloride and benzoylphosphamic chloride readily react with aniline. In each case one of the chlorine atoms attached to phosphorus is immediately replaced by the anilino-group, whilst the other tends to be eliminated more slowly as hydrogen chloride under the influence of the aniline, instead of being replaced. The final product of the action of aniline on *a*-chlorobenzylidenephosphamic chloride after several days is phenyliminophosphorylphenylbenzamidine, $C_6H_5{\cdot}C(NHPh){:}N{\cdot}PO{:}NPh$, and not the expected trianilino-derivative. The changes which have been observed are shown in the following scheme:



Steinkopf, to whose work reference has been made (*loc. cit.*), obtained, by the action of phosphorus pentachloride on halogen-substituted acetamides, phosphorus derivatives containing the grouping $\cdot CCl{:}N{\cdot}POCl_2$, but tacitly assumes that the production of such derivatives * is due to the influence of the halogen atoms in the substituted amides, and incidentally notes that benzamide and phosphorus pentachloride yield benzonitrile, apparently on Wallach's authority, which, however, is not justified. Having regard to the observations of Wallach, Steinkopf, and the authors, it would appear that the production of phosphorus derivatives may be expected with all primary amides; the simple derivatives containing the groups, $\cdot CCl_2{\cdot}NH_2$ and $\cdot CCl{:}NH$ may only be expected when catalytic influences are excluded, but the separation of such unstable derivatives from the accompanying phosphoryl chloride is usually impossible.

EXPERIMENTAL.

Action of Phosphorus Pentachloride on Benzamide, without Solvent.

1. *At* 8°.—An intimate mixture of very finely powdered benzamide (1·5 gram) and phosphorus pentachloride (2·6 grams) contained in a small tube, provided with a phosphoric oxide trap and delivery tube,

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* Steinkopf regards these compounds as phosphorous derivatives, his system of nomenclature, which is quite different from that adopted by the authors, having been devised to distinguish the constitution of such compounds from true phosphoric derivatives containing the grouping $\cdot O{\cdot}PO<$. Thus, he calls $CCl_3{\cdot}CCl{:}N{\cdot}POCl_2$, "trichloracetimid chlorid phosphorigsäure dichlorid," and $CCl_3{\cdot}CO{\cdot}NH{\cdot}POCl_2$, "trichloracetamid phosphorigsäure dichlorid." As, however, all these compounds and those of the authors, on hydrolysis, yield phosphoric acid and not phosphorous acid, the authors prefer to regard them as phosphamic derivatives.

was kept at 8° and the hydrogen chloride evolved was collected in water. In three hours action had ceased and a pale yellow liquid resulted. The hydrogen chloride absorbed by the water was titrated with alkali, and, after correcting for the volume of the apparatus, was found to be 0·38 gram (1 mol. = 0·45 gram HCl). The pale yellow liquid was apparently stable at 0°, and did not solidify at −22°. On exposure to atmospheric moisture it yielded a syrup consisting chiefly of benzonitrile and phosphoric acid, which were also formed on treatment with water; benzoylphosphamic chloride was not produced in appreciable quantity. Above 15° the liquid obtained at 8° steadily decomposed, evolving hydrogen chloride, and at 50° the decomposition was complete in five minutes. The hydrogen chloride evolved weighed 0·4125 gram (1 mol. = 0·45 gram HCl). The liquid remaining after heating at 50° was found to consist essentially of benzonitrile and phosphoryl chloride. In another experiment, using larger quantities, the liquid obtained at 8° was cooled to 0° and treated with light petroleum, which precipitated an almost colourless oil; this oil was washed at 0° by shaking repeatedly with small quantities of light petroleum in which, however, it was appreciably soluble. The washings contained phosphoryl chloride in quantity, which was shown by analysis after decomposition by water. The oil precipitated by the petroleum was not a pure substance and contained phosphorus, although in relatively small quantity, and the yield of the oil was small. A portion, after being kept in a vacuum for a short time, was analysed volumetrically by decomposing with water and titrating with sodium carbonate (using methyl-orange) and silver nitrate.

1·813 required 19·5 c.c. N-Na_2CO_3 and 168·5 c.c. $N/10$ $AgNO_3$.
$P = 4·6$; $Cl = 32·9$.

Assuming the phosphorus derivative (phosphoryl chloride, which is miscible with light petroleum, being excluded) to be (*a*)

$$C_6H_5{\cdot}CCl_2{\cdot}NH{\cdot}POCl_2,$$

or (*b*) $C_6H_5{\cdot}CCl{:}N{\cdot}POCl_2$, from the above values it is possible to calculate the net amount of chlorine in the remaining substance. This gives (*a*) $Cl = 21·02$ or (*b*) $Cl = 27·2$ per cent.

$C_6H_5{\cdot}CCl{:}NH$ requires $Cl = 25·44$ per cent.

Owing to the extremely easy decomposability of the substance, and the readiness with which benzonitrile is produced, on attempted purification no more satisfactory data than the above could be obtained. Besides benzonitrile and benzoylphosphamic acid, the oil gave on treatment with water a small quantity of a phosphorous acid derivative yielding dibenzamide on hydrolysis, which separated in needles (m. p. 148°) on heating the aqueous solution at 100° for about two hours.

2. *At* 15°.—The action between benzamide and phosphorus pentachloride was found to be very much more rapid at 15° than 8°, and only required from thirty to forty minutes for completion.

1·5 benzamide gave 0·510 HCl (1 mol. = 0·45 HCl).

The resulting pale yellow liquid neither solidified on cooling nor yielded crystals of benzoylphosphamic chloride on exposure to atmospheric moisture, even after previous admixture with benzene, or heating to 50°. In all its properties it was similar to the liquid obtained at 8°, although it probably contained relatively less α-chlorobenzimide, since at 15° hydrogen chloride was slowly but continuously disengaged.

3. *At* 50°.—In the action between benzamide and phosphorus pentachloride at 50° which was very vigorous, the hydrogen chloride amounted to 2 mols. and the action was complete in twelve minutes. The resulting pale yellow liquid was found to vary in composition and on cooling to − 20° sometimes set to an almost solid crystalline mass; in most cases it became viscous without solidifying. In all cases observed there appeared to be a considerable quantity of benzonitrile and phosphoryl chloride formed, but the main product was α-chlorobenzylidenephosphamic chloride. Attempts were made to isolate the latter in a pure condition by treatment with light petroleum at a low temperature but it was found impossible to remove the accompanying substances in this way. On exposure to air it rapidly absorbs moisture forming benzoylphosphamic chloride (m. p. 110°, see p. 1151) whilst on treatment with water it is instantly decomposed, yielding this compound as an insoluble white crystalline solid and benzoylphosphamic acid which is found in the aqueous solution. The variation in the composition of the liquid obtained in the reaction 50° was readily followed by noting the relative amounts of benzoylphosphamic chloride and benzonitrile obtained after exposure to air, the yield of phosphamic chloride being smaller the greater the lapse of time between mixing the benzamide and phosphorus pentachloride, and raising the temperature to 50°. In no case was the quantitative yield of the phosphamic chloride obtained.

Action of Phosphorus Pentachloride on Benzamide in Presence of a Solvent.

α-Chlorobenzylidenephosphamic Chloride, $C_6H_5\cdot CCl:N\cdot POCl_2$.

1. *Using Chloroform.*—A vigorous action took place in the cold with evolution of hydrogen chloride, and the resulting chloroform solution on exposure deposited a large amount of benzoylphosphamic

chloride in colourless plates, together with a relatively small quantity of a syrup consisting of benzonitrile and phosphoric acid. The hydrogen chloride evolved in the action in the cold was not measured, owing to its moderate solubility in chloroform. At 60° it amounted to 75 per cent. of the theoretical quantity for two molecules, and 2·7 grams of benzoylphosphamic chloride were obtained from 3 grams of benzamide. Several attempts were made to obtain pure α-chlorobenzylidenephosphamic chloride, using the chloroform method by modifying the conditions, but in all cases some benzonitrile and phosphoryl chloride were formed.

By using a small quantity of chloroform in the reaction at 50°, and subsequently heating in a vacuum at 60°, an oil was obtained consisting chiefly of α-chlorobenzylidenephosphamic chloride, but containing some benzonitrile:

2·382 required 29·59 c.c. N-Na_2CO_3 and 225·5 c.c. $N/10$-$AgNO_3$.

Ratio, P : Cl = 1 : 3·2 ; P = 9·1 ; Cl = 34·6.

These figures correspond with a mixture of 84 per cent. of α-chlorobenzylidenephosphamic chloride and 16 per cent. of benzonitrile.

In another experiment a purer product was obtained by using only a trace of chloroform at 50°, and proceeding as before. The benzonitrile it contained was determined and corrected for:

2·3538 gave 0·159 $C_6H_5{\cdot}CN$ and 0·8830 $Mg_2P_2O_7$.

2·3538 required 235·0 c.c. $N/10$ $AgNO_3$.

P = 11·24 ; Cl = 38·01. (After correcting for $C_6H_5{\cdot}CN$.)

$C_7H_5ONCl_3P$ requires P = 12·09 ; Cl = 41·53 per cent.

The low chlorine value is attributed to the loss of hydrogen chloride, due to moisture, which it is almost impossible to exclude during the treatment in a vacuum.

2. *Using Benzene.*—The same results were obtained as with chloroform, and the method employed was similar:

3·0 benzamide gave (1) 1·022 HCl at 15°, and (2) 1·60 HCl at 50°.

(1) 1 mol. HCl = 0·92, and (2) 2 mols. HCl = 1·84.

By carrying out the reaction at 50° in presence of a small quantity of benzene, an oil was obtained after heating at 60° in a vacuum, which on analysis was found to contain 90 per cent. of α-chlorobenzylidenephosphamic chloride. In the reaction at 15° from 3·4 grams of benzamide, 4 grams of benzoylphosphamic chloride were obtained by exposure to moist air immediately the reaction was over; by previously keeping for twenty-four hours at 15°, however, the yield of benzoylphosphamic chloride was very much diminished, and a correspondingly large amount of benzonitrile was obtained. It would seem, therefore, that the first product of the reaction, αα-dichlorobenzylphosphamic chloride, slowly decomposes in benzene solution at the ordinary temperature into benzonitrile and phosphoryl chloride.

Benzoylphosphamic Chloride, $C_6H_5 \cdot CO \cdot NH \cdot POCl_2$.

An intimate mixture of 24·2 grams of finely-powdered benzamide and 41·8 grams of phosphorus pentachloride was rapidly treated with 100 grams of pure benzene, and the mixture immediately heated in a bath at 50°. After twenty minutes the action, which was very vigorous, was complete, and the liquid was exposed to air in a shallow dish for twelve hours. Masses of large, colourless crystals continually separated as moisture was absorbed, and finally a practically dry solid was left. The crystals were quickly washed with cold water and dried at room-temperature on porous porcelain. They melted at 110°, and weighed 43·5 grams (theory requires 47·6 grams). The substance was quite pure. Prepared by a similar method to the above, using chloroform instead of benzene, a smaller yield was obtained:

0·3138 required 38·2 c.c. $N/10$-Na_2CO_3 and 26·0 c.c. $N/10$-$AgNO_3$.
Ratio, $P : Cl = 1 : 2{\cdot}1$; $Cl = 29{\cdot}42$.

0·4654 required 58·0 c.c. $N/10$-Na_2CO_3 and 38·5 c.c. $N/10$-$AgNO_3$.
Ratio, $P : Cl = 1 : 1{\cdot}97$; $Cl = 29{\cdot}36$.

0·6324 gave 0·2894 $Mg_2P_2O_7$; $P = 12{\cdot}77$.

1·1098, by Kjeldahl's method, required 47·6 c.c. $N/10.HCl$; $N = 6{\cdot}00$.

$C_7H_6O_2NCl_2P$ requires $P = 13{\cdot}02$; $Cl = 29{\cdot}8$; $N = 5{\cdot}88$ per cent.

Benzoylphosphamic chloride crystallises in colourless plates melting at 115° when pure and rapidly heated, but usually at 110° owing to decomposition, which begins even below 100°. When heated at 120°, hydrogen chloride is rapidly evolved, the decomposition is complete in fifteen minutes, and the liquid separates into two layers, the upper consisting of benzonitrile and phosphoryl chloride, the lower of phosphoric acid. Owing to its easy decomposition, benzoylphosphamic chloride could not be satisfactorily recrystallised from hot solvents. It is practically insoluble in cold benzene or light petroleum, sparingly soluble in hot benzene, cold alcohol, ether, or chloroform, and moderately so in acetone; the solutions readily decompose in presence of moisture with formation of benzoylphosphamic acid. A similar decomposition occurs slowly with the pure dry substance, which on this account cannot be kept long in ordinary moist air. On the other hand, treatment with cold water has no appreciable action on the substance, which is insoluble, but when boiled in water it is rapidly and completely decomposed into hydrochloric and phosphoric acids and benzamide, which crystallises out on cooling.

Benzoylphosphamic chloride is immediately decomposed in the cold by alkalis, even by aqueous sodium hydrogen carbonate (with effervescence) and sodium acetate, yielding a salt of benzoylphosphamic acid; when treated with sodium hydroxide, three molecular equivalents of the latter are required for neutralisation, using methyl-orange, and four using phenolphthalein as indicators.

By treatment with aniline it yields different derivatives, according to conditions.

Phenyliminophosphorylbenzamide, $C_6H_5\cdot CO\cdot NH\cdot PO\colon NPh \rightleftharpoons C_6H_5\cdot C(OH)\colon N\cdot PO\colon NPh$.

Five grams of benzoylphosphamic chloride, suspended in 30 c.c. of water, were treated with 8 grams of aniline, and the mixture was well triturated. The thin, oily emulsion first formed rapidly hardened, and in a few minutes voluminous white masses of a granular solid separated. After thirty minutes the whole was stirred with dilute hydrochloric acid, and the insoluble portion was collected and crystallised from alcohol. The pure substance separated in colourless, silky needles, melting at 226°, and weighed 5·4 grams (yield theoretical):

0·4944, by Kjeldahl's method, required 37·1 c.c. *N*/10-HCl. N = 10·55.
0·4368 ,, ,, ,, ,, 33·7 c.c. *N*/10-HCl. N = 10·82.
0·3458 gave 0·1580 $Mg_2P_2O_7$. P = 12·55.
$C_{13}H_{11}O_2N_2P$ requires N = 10·85; P = 12·01 per cent.

Phenyliminophosphorylbenzamide is sparingly soluble in alcohol, ether, benzene or carbon tetrachloride and moderately so in acetone, chloroform or methyl alcohol. It is insoluble in aqueous sodium carbonate, but completely soluble in dilute sodium hydroxide and is reprecipitated by acids from the alkaline solution, in a gelatinous form melting at about 226°. This behaviour with alkali is similar to that of dibenzamide and indicates a similarity between the groups ·CO·NHPO· and ·CO·NH·CO. Like dibenzamide also, the compound is soluble in an excess of concentrated ammonia, although it is not changed on heating with this solvent. The tautomeric form, corresponding with the salts to which the compound gives rise must be regarded as $C_6H_5\cdot C(OH)\colon N\cdot PO\colon NPh$ and not the alternative form $C_6H_5\cdot CO\cdot N\colon P(OH)\colon NPh$, which should represent an acid soluble in sodium carbonate.

Benzoylaminoanilinophosphoryl Chloride, $C_6H_5\cdot CO\cdot NH\cdot POCl\cdot NHPh$.

4·8 Grams of benzoylphosphamic chloride suspended in 50 c.c. of absolute ether were treated with 7 grams of pure aniline and the mixture was shaken and kept for twelve hours. A large quantity of white solid matter was deposited; this was washed with ether, and treated as described below. The ethereal filtrate on evaporation left a white solid consisting of a mixture of phenyliminophosphorylbenzamide and an unstable substance, which were separated by digestion with 1 per cent. sodium hydroxide, in which the former is immediately, and the latter only slowly, soluble. By quickly washing and drying on porous porcelain it was obtained in an approximately pure state, but by crystallisation from alcohol or other solvents it was converted into phenyliminophosphorylbenzamide (m. p. 226°). As an analysis of the unpurified substance gave $N = 12{\cdot}27$ it probably consisted of the dianilino-derivative, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}PO(NHPh)_2$ ($N = 11{\cdot}96$ per cent.), but this could not be verified.

The insoluble solid obtained above in the action of aniline on benzoylphosphamic chloride was washed with water to remove aniline hydrochloride, and the residue, weighing 4·1 grams, consisting of nearly pure benzoylaminoanilinophosphoryl chloride was crystallised from alcohol, from which it separated in fine, silky needles melting at 176°.

0·1298 gave 11·4 c.c. N_2 (moist) at 24° and 747 mm.; $N = 9{\cdot}66$.
0·2682 „ 0·1282 AgCl; $Cl = 11{\cdot}83$.
$C_{13}H_{12}O_2N_2ClP$ requires $N = 9{\cdot}51$; $Cl = 12{\cdot}05$ per cent.

The chloro-derivative is moderately soluble in methyl or ethyl alcohol or acetone, and sparingly so in ether, benzene or chloroform. With aniline it reacts at once giving phenyliminophosphorylbenzamide, and it dissolves readily and decomposes in sodium hydroxide. The alkaline solution on acidifying deposits, after a few minutes, fine, colourless needles, appreciably soluble in cold water. The substance, which melts at 162°, does not contain chlorine, and as it is soluble with effervescence in sodium hydrogen carbonate it probably consists of the acid, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}PO(NHPh)OH$, but it was not obtained in sufficient quantity for analysis.

Benzoylphosphamic Acid, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}PO(OH)_2$.

This acid was prepared by dissolving benzoylphosphamic chloride in pure acetone, adding the calculated amount of water and allowing the solution to evaporate. Transparent crusts of crystals slowly separated consisting of the nearly pure acid, the yield being almost theoretical. After crystallisation from methyl alcohol containing benzene it melted at 157—158°.

0·4572 gave 0·2582 $Mg_2P_2O_7$; $P = 15{\cdot}69$.
0·3933 by Kjeldahl's method required 20·3 c.c.; $N/10$-HCl; $N = 7{\cdot}23$.
$C_7H_8O_4NP$ requires $P = 15{\cdot}43$; $N = 6{\cdot}96$ per cent.

Benzoylphosphamic acid is readily soluble in water, methyl or ethyl alcohol, sparingly so in acetone, and insoluble in benzene, ether, chloroform, or ethyl acetate. On boiling with water for a few minutes it is completely decomposed into benzamide and phosphoric acid. A neutral solution of the ammonium salt gives a nearly white precipitate with ferric chloride and voluminous, white precipitates with silver nitrate, barium chloride and calcium chloride but no precipitate with magnesia mixture. The free acid, like phosphoric acid, requires one molecular equivalent of sodium hydroxide for neutralisation, using methyl-orange as indicator, and two using phenolphthalein.

Phenyliminophosphorylphenylbenzamidine, $C_6H_5 \cdot C(NHPh)\colon N \cdot PO\colon NPh$.

When aniline was allowed to act on α-chlorobenzylidenephosphamic chloride in benzene solution for twenty-four hours and the clear filtrate from the aniline hydrochloride was left exposed to air a mixture was gradually deposited consisting of phenyliminophosphorylbenzamide (m. p. 226°) and phenyliminophosphorylphenylbenzamidine (m. p. 227°) which were readily separated by treatment with dilute sodium hydroxide, the compound melting at 227° being insoluble. A better yield of the latter was obtained by allowing the aniline to act for a longer time.

A mixture of 9 grams of benzamide, 15·5 grams of phosphorus pentachloride, and 20 grams of pure benzene was rapidly placed in a bath at 50°, and kept at this temperature for forty minutes until action had ceased. The resulting solution of α-chlorobenzylidenephosphamic chloride was cooled to 0° and treated gradually with 50 grams of pure aniline and kept for forty-eight hours. The insoluble aniline hydrochloride was collected and the filtrate left in an open dish for twelve hours. A white solid (30 grams) was deposited which was collected and washed with benzene. This solid was a mixture and contained chlorine; on keeping its alcoholic solution *phenyliminophosphorylphenylbenzamidine* (13 grams) was deposited as a white, microcrystalline powder. On recrystallisation from boiling alcohol, in which it is not very soluble, it was obtained in fine needles melting at 227—228°:

0·2531 gave 0·0872 $Mg_2P_2O_7$, and required 22·4 c.c. *N*/10-HCl; $P = 9{\cdot}62$; $N = 12{\cdot}39$.

$C_{19}H_{16}ON_3P$ requires $P = 9{\cdot}31$; $N = 12{\cdot}61$ per cent.

The compound is sparingly soluble in methyl or ethyl alcohol or chloroform and practically insoluble in ether, benzene, or carbon tetrachloride. It is moderately soluble in acetone, and separates as a mealy powder on adding a small quantity of water to the hot solution.

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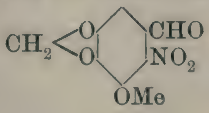
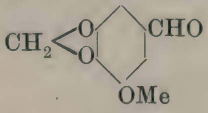
CXXX.—*The Action of Nitric Acid on the Ethers of Aromatic Hydroxyaldehydes.*

By Arthur Henry Salway.

In the course of some experiments on the synthesis of substances allied to cotarnine, the author had occasion to prepare a compound of the formula (I), and an attempt was made to achieve this object by the action of nitric acid on myristicinaldehyde (II). The yield of the desired nitroaldehyde was comparatively small, the principal product of the reaction being a neutral nitro-compound, which did not contain an aldehyde group, and was found to consist of a nitromethoxymethylenedioxybenzene. The formation of the latter compound from myristicinaldehyde is evidently due to the elimination of the aldehyde group and the introduction of a nitro-group into the nucleus.



(I.)

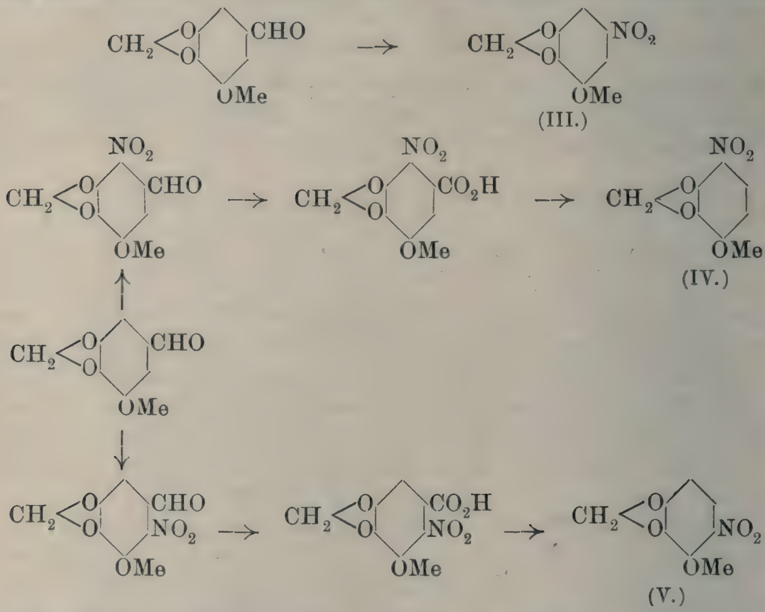


(II.)

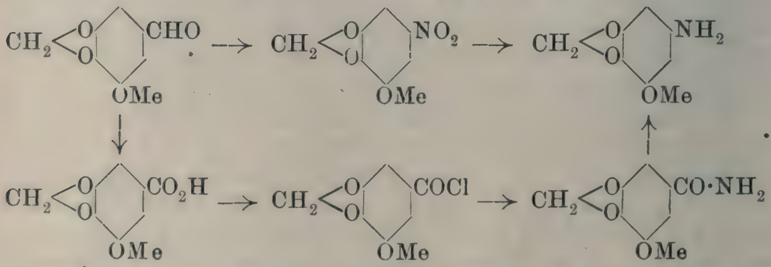
It will be seen that the orientation of the nitro-group in this nitromethoxymethylenedioxybenzene is essential for the correct interpretation of the manner in which the aldehyde group is eliminated. Thus it might be supposed, on the one hand, that the aldehyde group undergoes direct substitution by a nitro-group, in which case the constitution of the resulting nitro-compound would be represented by formula (III); on the other hand, it is conceivable that the myristicinaldehyde primarily undergoes nitration with the formation of nitromyristicinaldehyde, which, by oxidation to the corresponding nitrocarboxylic acid and subsequent liberation of carbon dioxide, becomes converted into a nitromethoxymethylenedioxybenzene. In this case the constitution of the latter would be represented by (IV) or (V).

The formation of nitromyristicinaldehyde as one of the products of the nitration of myristicinaldehyde lends some degree of probability to the latter view. However, on further oxidising nitromyristicinaldehyde, the only product was the stable nitromyristicinic acid, and there was no evidence of the formation of nitromethoxymethylenedioxybenzene. It appeared, therefore, improbable that this compound owes its formation to the intermediate production of nitromyristicinaldehyde according to (IV) or (V), and it was subsequently proved beyond question by the following series of reactions that nitromethoxymethylenedioxybenzene is produced by the direct substitution of the aldehyde group according to (III).

Myristicinaldehyde was converted, on the one hand, by means of nitric acid into nitromethoxymethylenedioxybenzene—the constitution of which was to be determined—and the latter reduced to the corresponding amino-derivative; on the other hand, myristicinaldehyde was

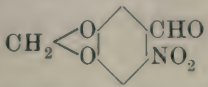


oxidised to myristicinic acid, which, after successive transformation into the chloride and amide, was finally converted into 5-amino-1-methoxy-2 : 3-methylenedioxybenzene, the constitution of which follows from that of myristicinaldehyde. The amines obtained in these two series of reactions were identical and gave identical derivatives:

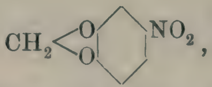


It next seemed of interest to ascertain whether the displacement of the aldehyde group by a nitro-group is a reaction common to the alkyl ethers of aromatic hydroxyaldehydes. Piperonal (Fittig and Remsen, *Annalen*, 1871, **159**, 34), vanillin methyl ether (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3405), and anisaldehyde (Einhorn and

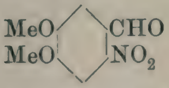
Grabfield, *Annalen*, 1888, **243**, 370) have already been subjected by the above-mentioned investigators to the action of concentrated nitric acid; in each case the corresponding nitroaldehydes were obtained, but the formation of nitroalkyloxybenzenes was not observed. On repeating these experiments it was found, however, that both piperonal and vanillin methyl ether exhibit the same behaviour towards nitric acid as myristicinaldehyde, that is to say, part of the aldehyde is directly nitrated, whilst the remainder undergoes nitration with elimination of the aldehydic group. Thus piperonal is converted by nitric acid at 0° into a mixture of nitropiperonal and 4-nitro-1:2-methylenedioxybenzene:



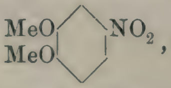
and



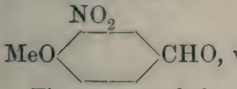
the separation of which was easily effected by means of sodium hydrogen sulphite. Vanillin methyl ether, under similar conditions yielded a mixture of nitrovanillin methyl ether and 4-nitroveratrole:



and

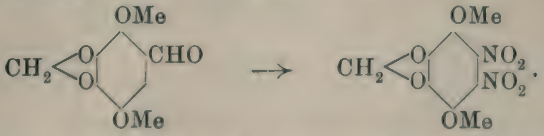


Anisaldehyde, on the other hand, was converted into nitroanisaldehyde,



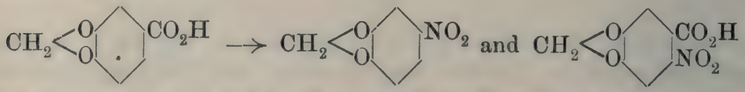
without the formation of any *p*-nitroanisole.

The results of the above experiments on the nitration of the alkyl ethers of aromatic hydroxyaldehydes also serve to elucidate the hitherto unexplained observations of Ginsberg (*Ber.*, 1888, **21**, 108) respecting the action of nitric acid on apiolaldehyde. In this case a nitro-compound melting at 116° was obtained, to which no formula could be assigned. With consideration of the analytical data recorded by Ginsberg in connexion with this nitro-compound and its derivatives, it is now evident that the substance melting at 116° is dinitroapione, and that it was formed from apiolaldehyde by removal of the aldehyde group with simultaneous nitration:

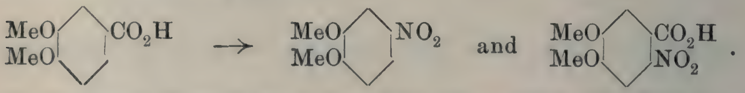


It is worthy of note that with the accumulation of alkyloxy-groups the elimination of the aldehyde group on nitration takes place with greater readiness, and that the formation of the nitroalkyloxybenzaldehyde is inhibited in a corresponding degree. Thus the formation of 5-nitro-1-methoxy-2:3-methylenedioxybenzene from myristicinaldehyde takes place to the extent of 60·6 per cent. Piperonal, on the other hand, yields only 30 per cent. of 4-nitro-1 : 2-methylenedioxybenzene, whilst with anisaldehyde substitution of the aldehydic group does not occur.

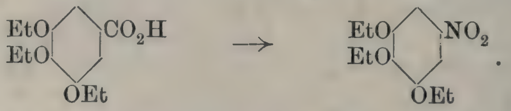
Although the direct displacement of the aldehydic group of the ethers of aromatic hydroxyaldehydes by the nitro-group has not hitherto been observed, an analogous transformation, in which the carboxyl group of the corresponding ethers of aromatic hydroxy-acids is eliminated with simultaneous nitration, has long been on record. Thus Jobst and Hesse (*Annalen*, 1879, **199**, 70) have shown that when piperonylic acid is acted on by concentrated nitric acid, it is converted into a mixture of 4-nitro-1 : 2-methylenedioxybenzene and nitropiperonylic acid:



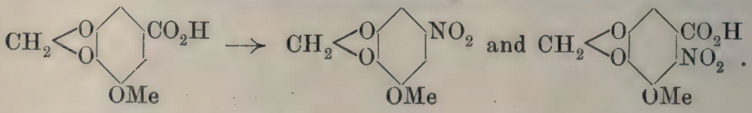
A similar reaction has been observed by Tiemann (*Ber.*, 1876, **9**, 936) in the case of veratric acid, which yields on nitration 4-nitroveratrole and nitroveratric acid:



Furthermore, Weselsky and Benedikt (*Ber.*, 1892, **25**, 722) have shown that the triethyl ether of gallic acid is almost quantitatively converted by nitric acid into 5-nitropyrogallol triethyl ether:



In addition to these observations, the present author has investigated the action of nitric acid on myristicinic acid, and has found that a similar reaction ensues with the formation of a mixture of 5-nitro-1-methoxy-2 : 3-methylenedioxybenzene and nitromyristicinic acid:*



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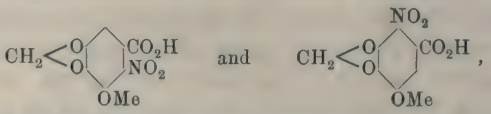
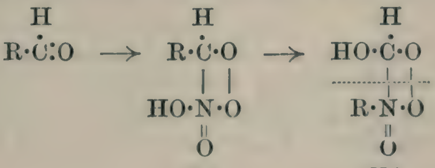
* Of the two possible formulæ for nitromyristicinic acid, namely:



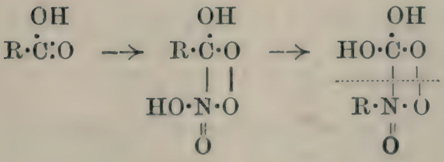
the former has been adopted throughout this communication, and the same applies in the case of nitromyristicinaldehyde.

In consideration of the fact that the ethers of aromatic hydroxyaldehydes, under the influence of nitric acid, show the same transformation as the corresponding carboxylic acids, it might at first be supposed that the reaction in the case of the former depended primarily on their oxidation to the latter. That this view, however, is untenable is evident from the following considerations based on experiments with myristicinaldehyde and myristicinic acid. When myristicinic acid is acted on by nitric acid in the cold, the chief product is 5-nitro-1-methoxy-2 : 3-methylenedioxybenzene, but some nitromyristicinic acid is always formed. If, therefore, myristicinic acid is an intermediate product in the action of nitric acid on myristicinaldehyde, nitromyristicinic acid would be formed in this reaction. As a matter of fact, however, no acid whatsoever is produced. For this reason it would seem that the carbonyl group, which is common to both series of compounds, is alone responsible for the reaction, and that any explanation of the mechanism of the transformation must be sought for in the action of nitric acid on this group. Although there is at present no direct evidence on which the mechanism of the reaction may be based, the following explanation may be suggested. In the first place it is conceivable that the carbonyl of the aldehyde group forms with nitric acid an additive product (I), which subsequently undergoes a change analogous to the Beckmann transformation. The resulting substance (II) is, however, unstable, and decomposes, as indicated by the dotted line below, with the formation of a substituted nitrobenzene and formic acid, the latter in the presence of nitric acid being oxidised to carbon dioxide.



$$\begin{array}{c}H\\R\cdot\dot{C}\colon O\end{array}\longrightarrow\begin{array}{c}H\\R\cdot\dot{C}\cdot O\\|\ \ |\\HO\cdot N\cdot O\\\Vert\\O\end{array}\longrightarrow\begin{array}{c}H\\HO\cdot\dot{C}\cdot O\\|\ \ |\\R\cdot N\cdot O\\\Vert\\O\end{array}$$

(I.) (II.)



$$\begin{array}{c}OH\\R\cdot\dot{C}\colon O\end{array}\longrightarrow\begin{array}{c}OH\\R\cdot\dot{C}\cdot O\\|\ \ |\\HO\cdot N\cdot O\\\Vert\\O\end{array}\longrightarrow\begin{array}{c}OH\\HO\cdot\dot{C}\cdot O\\|\ \ |\\R\cdot N\cdot O\\\Vert\\O\end{array}$$

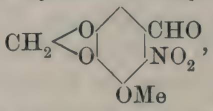
EXPERIMENTAL.

Action of Concentrated Nitric Acid on Myristicinaldehyde.

One part of finely divided myristicinaldehyde was added in small quantities at a time to 7 parts of nitric acid (sp. gr. 1·42) at 0°. The myristicinaldehyde gradually passed into solution, and after a short time carbon dioxide was slowly evolved. The mixture was kept at 0° for an hour, then poured into ice-water, and the yellow precipitate collected and washed free from nitric acid. It was then shaken with an excess of aqueous sodium hydrogen sulphite, by means of which a separation into a soluble and an insoluble portion was effected. The soluble portion was reprecipitated by adding dilute aqueous sodium hydroxide, collected, and washed. The yield of this substance amounted to 39·4 per cent. of the myristicinaldehyde employed. It was crystallised from alcohol, and was obtained in well-formed, prismatic needles, melting at 131—132°:

0·1134 gave 0·2000 CO_2 and 0·0360 H_2O. C = 48·1; H = 3·5.
$C_9H_7O_6N$ requires C = 48·0; H = 3·1 per cent.

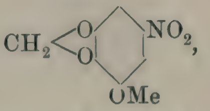
The analysis and chemical behaviour of this compound show that it is a mononitro-derivative of myristicinaldehyde.

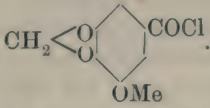
Nitromyristicinaldehyde, , is easily soluble in the usual organic solvents with the exception of light petroleum. It is readily soluble in aqueous sodium hydrogen sulphite, giving a deep yellow solution. When freshly crystallised from alcohol it is practically colourless, but on exposure to light quickly becomes deep yellow. When oxidised with alkaline permanganate it is converted into nitromyristicinic acid, which melts and decomposes at 245°, and is identical with the acid obtained by the nitration of myristicinic acid (p. 1165).

The portion of the product of the action of nitric acid on myristicinaldehyde which was insoluble in sodium hydrogen sulphite amounted to 60·6 per cent. of the aldehyde employed. It was purified by crystallisation from alcohol, from which it separated in long, almost colourless needles, melting at 143—144°:

0·1386 gave 0·2481 CO_2 and 0·0481 H_2O. C = 48·8; H = 3·9.
0·2928 ,, 17·5 c.c. N_2 at 20° and 766 mm.. N = 6·9.
$C_8H_7O_5N$ requires C = 48·7; H = 3·6; N = 7·1 per cent.

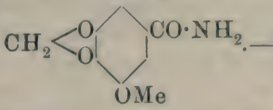
It is evident that the formation of a compound, $C_8H_7O_5N$, from myristicinaldehyde could only be brought about by the elimination of the aldehydic group and simultaneous introduction of a nitro-group into the molecule. The substance melting at 143—144° must be, therefore, a nitromethoxymethylenedioxybenzene. As explained in the introduction, of the three possible nitro-1-methoxy-2 : 3-methylenedioxybenzenes, the present one must contain the nitro-group in the 5-position.

5-*Nitro*-1-*methoxy*-2 : 3-*methylenedioxybenzene*,  is readily soluble in alcohol, ethyl acetate, or benzene, from each of which it crystallises in long, almost colourless needles. It may readily be sublimed when heated above its melting point. When warmed with alcoholic potash it is hydrolysed to the corresponding nitrophenol, 5-*nitro*-1-*hydroxy*-2 : 3-*methylenedioxybenzene*, which crystallises from water in yellow, silky needles melting at 94°, and is soluble in alkalis with a deep red colour. In determining the constitution of 5-nitro-1-methoxy-2 : 3-methylenedioxybenzene it wa necessary, as already explained, to prepare successively myristicino chloride, myristicinamide, and 5-amino-1-methoxy-2 : 3-methylene dioxybenzene. Since these substances have not hitherto been described, the method of preparation, together with their characteristic properties, may briefly be indicated.

Myristicinoyl Chloride, .—A mixture of myristicinic acid (1 mol.) and phosphorus pentachloride (1 mol.) was heated for a short time at 100°. After removal of the phosphoryl chloride, the product was purified by distillation under diminished pressure. *Myristicinoyl chloride* distils at 189—190°/20 mm. as a colourless oil, which rapidly solidifies, and crystallises from a mixture of benzene and light petroleum in long, thin, colourless needles melting at 105° :

0·3236 gave 0·2200 AgCl. Cl = 16·8.

$C_9H_7O_4Cl$ requires Cl = 16·6 per cent.

Myristicinamide, .—To a solution of myristicinoyl chloride in benzene an excess of concentrated ammonia was added, and the mixture vigorously shaken. The precipitated amide was collected, and recrystallised from hot water, in which it is only moderately soluble. It separated in long, thin needles, which contain one molecule of water of crystallisation, and melts at 184°. It is readily soluble in hot alcohol, from which it is deposited in clusters of feathery needles :

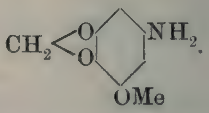
0·7164 lost, at 105°, 0·0631 H_2O. H_2O = 8·8.

0·1485 gave 0·3028 CO_2 and 0·0660 H_2O. C = 55·6 ; H = 4·9.

$C_9H_9O_4N,H_2O$ requires H_2O = 8·5 per cent.

$C_9H_9O_4N$ requires C = 55·4 ; H = 4·6 per cent.

5-*Amino*-1-*methoxy*-2 : 3-*methylenedioxybenzene*,



(*a*) *Preparation from Myristicinamide.*—Finely powdered myristicinamide was shaken continuously for several hours with the theoretical quantity of a freshly-prepared solution of sodium hypochlorite (compare Graebe, *Ber.*, 1902, **35**, 2753), and the mixture nally heated at 100° for a short time. The product was then cooled nd extracted with ether, when the ethereal solution, after evaporation, lded an oily residue, which soon solidified. It was purified by stallisation from water, from which it separated in colourless aflets, melting at 85—86°:

0·1076 gave 0·2263 CO_2 and 0·0553 H_2O. C = 57·4; H = 5·7.

$C_8H_9O_3N$ requires C = 57·5; H = 5·4.

(*b*) *Preparation from* 5-*Nitro*-1-*methoxy*-2 : 3-*methylenedioxybenzene.*—To 1 part of the finely divided nitro-compound 5 parts of stannous chloride in 15 parts of concentrated hydrochloric acid were added, and the mixture was gently warmed for one hour. A crystalline tin double salt of the amino-compound was formed, from which the tin was removed by means of hydrogen sulphide. The aqueous solution was then concentrated to a small bulk, rendered alkaline with sodium carbonate, and extracted with ether; the ethereal solution, after evaporation, left a residue which rapidly solidified and was crystallised from hot water, when it was deposited in colourless leaflets melting at 85—86°. When this substance was mixed with the 5-amino-1-methoxy-2 : 3-methylenedioxybenzene, prepared from myristicinamide as above described, the melting point remained unchanged. Further confirmation of the identity of the two products was obtained by the preparation from each of the same benzoyl derivative, melting at 128—129°.

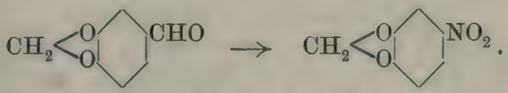
5-*Amino*-1-*methoxy*-2 : 3-*methylenedioxybenzene* is readily soluble in benzene, ether, chloroform, ethyl acetate, or alcohol, but only sparingly soluble in light petroleum. It is best crystallised from hot water, but can also be crystallised from a mixture of benzene or alcohol and petroleum. Its *hydrochloride* crystallises from dilute alcohol in well-formed, colourless needles, which decompose at about 245°. It yields a *benzoyl* derivative, which crystallises from alcohol in colourless rosettes of feathery needles melting at 128—129°:

0·1136 gave 0·2770 CO_2 and 0·0506 H_2O. C = 66·5; H = 4·9.

$C_{15}H_{13}O_4N$ requires C = 66·4; H = 4·8 per cent.

Formation of 4-*Nitro*-1 : 2-*methylenedioxybenzene by the Action of Nitric Acid on Piperonal.*

The action of nitric acid on piperonal was first investigated by Fittig and Remsen (*Annalen*, 1871, **159**, 134), who isolated only nitropiperonal from the product of the reaction. This experiment has been repeated in order to ascertain whether, in addition to the formation of nitropiperonal, any portion of the piperonal is converted into 4-nitro-1 : 2-methylenedioxybenzene by elimination of the aldehydic group :



For this purpose 5 grams of finely divided piperonal were added in small quantities at a time to 50 c.c. of nitric acid (sp. gr. 1·41) at 0°. Each addition of piperonal immediately conglomerated to a solid cake, which was broken up by means of a glass rod. After all the piperonal had been added, the mixture was well shaken from time to time until complete solution was effected, for which about an hour was necessary. The mixture was then poured into ice-water, the yellow precipitate collected, washed free from nitric acid, and then shaken with a solution of sodium hydrogen sulphite. In this manner the product was separated into a soluble aldehydic portion and an insoluble neutral portion. The soluble portion was reprecipitated by adding alkali hydroxide, when it amounted to 3·6 grams, corresponding with a yield of 70 per cent. When crystallised from a mixture of alcohol and ethyl acetate, it was obtained in stout, yellow needles melting at 98°. This was identical with the nitropiperonal (m. p. 95·5°) described by Fittig and Remsen (*loc. cit.*). The portion insoluble in sodium hydrogen sulphite amounted to 1·5 grams, representing a yield of 30 per cent. When crystallised from hot alcohol it separated in long, yellow needles melting at 145°, and this melting point was not changed on recrystallisation :

0·2241 gave 16·1 c.c. N_2 at 16·5° and 767 mm.. $N = 8·5$.

$C_7H_5O_4N$ requires $N = 8·4$ per cent.

This substance is therefore identical with the 4-nitro-1 : 2-methylenedioxybenzene (m. p. 148°) described by Jobst and Hesse (*Annalen*, 1879, **199**, 70).

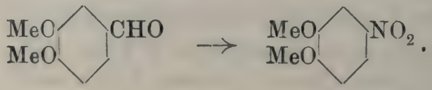
Formation of 4-*Nitroveratrole by the Action of Nitric Acid on Vanillin Methyl Ether.*

Five grams of vanillin methyl ether were gradually added to 50 c.c. of nitric acid (sp. gr. 1·41) at 0°. After one hour the mixture was poured into cold water, the voluminous, yellow precipitate collected, washed with water, and shaken with a solution of sodium hydrogen sulphite. The soluble substance amounted to 94 per cent. of the aldehyde employed. When crystallised from alcohol it separated in yellow needles melting at 134°, and was identical with the nitrovanillin methyl ether of Pschorr and Sumuleanu (*Ber.*, 1899, **32**, 3405). The portion insoluble in sodium hydrogen sulphite amounted to 6 per cent. of the weight of the aldehyde employed. It crystallised from alcohol in stout, deep yellow needles, melting at 96°:

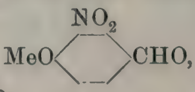
0·2548 gave 16·7 c.c. N_2 at 17° and 759 mm. N = 7·6.

$C_8H_9O_4N$ requires N = 7·7 per cent.

This substance is evidently 4-nitroveratrole (Tiemann, *Ber.*, 1876, **9**, 939; 1878, **11**, 131), and its formation is due to the direct displacement of the aldehydic group of vanillin methyl ether by a nitro-group:



Action of Nitric Acid on Anisaldehyde.

When anisaldehyde is treated with nitric acid at 0° under the same conditions as those described in connexion with the nitration of myristicinaldehyde, piperonal, etc., it first dissolves, and then immediately crystallises unchanged in long, colourless needles, which are only slowly attacked by the nitric acid. At the ordinary temperature, however, nitration takes place with greater readiness. The reaction was therefore conducted as follows: 5 grams of anisaldehyde were added, drop by drop, to 50 c.c. of concentrated nitric acid (sp. gr. 1·41) at the ordinary temperature; after about four hours, water was added, and the precipitated oil extracted with ether. The ethereal solution was first shaken with aqueous sodium hydrogen sulphite until free from aldehyde, then with dilute sodium carbonate, which removed a small quantity of anisic acid, and finally washed with a little water. After drying and removing the ether, no trace of *p*-nitroanisole was obtained. The aldehydic group of anisaldehyde is therefore not eliminated by the action of nitric acid in the cold. The portion of the product which had been extracted with sodium hydrogen sulphite was precipitated as a yellow solid by the addition of sodium hydroxide. This was collected, washed, and crystallised from alcohol, when long, colourless needles melting at 84° were obtained. It was identified as mononitroanisaldehyde,  by conversion into its hydrazone melting at 132°:

0·0513 gave 0·1170 CO_2 and 0·0240 H_2O. C = 62·2; H = 5·2.

$C_{14}H_{13}O_3N_3$ requires C = 62·0; H = 4·8 per cent.

Einhorn and Grabfield (*Annalen*, 1888, **243**, 370), who first prepared mononitroanisaldehyde, assign to it a melting point of 83·5°, whilst, according to Wörner (*Ber.*, 1896, **29**, 157), it melts at 72°, and dinitroanisaldehyde at 86°. The above results confirm Einhorn and Grabfield's observation, and indicate that the correct melting point of nitroanisaldehyde is 84°.

The Action of Nitric Acid on Myristicinic Acid.

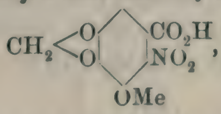
Twenty grams of myristicinic acid were gradually stirred into 300 c.c. of nitric acid (sp. gr. 1·41) at 0°. After a short time there was a vigorous evolution of carbon dioxide. The mixture was kept cold for an hour, then poured into ice-water, and the resulting precipitate collected and washed. By shaking with an aqueous solution of sodium carbonate, the product of the reaction was separated into a neutral and an acidic portion. The neutral portion amounted to 11·5 grams, corresponding to a yield of 57·5 per cent. It was crystallised from alcohol, when it was obtained in long needles melting at 143—144°. The substance was identical with the 5-nitro-1-methoxy-2:3-methylenedioxybenzene previously obtained by the nitration of myristicinaldehyde. The portion soluble in sodium carbonate was reprecipitated by the addition of dilute sulphuric acid, collected, and washed, when it amounted to 6·5 grams, representing a yield of 33·5 per cent. On recrystallisation from glacial acetic acid, it was deposited in radiating clusters of light yellow needles, which melted and decomposed at about 245°:

0·1667 gave 0·2746 CO_2 and 0·0450 H_2O. C = 44·9; H = 3·0.

0·2780 required 11·55 N/10-KOH for neutralisation. M.W. = 240·7

$C_9H_7O_7N$ requires C = 44·8; H = 2·9 per cent. M.W. = 241.

This substance is evidently a mononitromyristicinic acid.

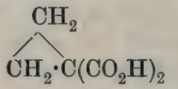
Nitromyristicinic acid,  is readily soluble in alcohol, ethyl acetate, or glacial acetic acid, but only sparingly so in benzene, chloroform, or hot water. From the latter it crystallises in colourless, silky needles, which slowly become yellow on exposure to light.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

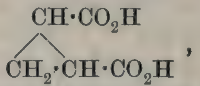
CXXXI.—cyclo*Butane*-1: 3-*dicarboxylic Acid and Some of its Derivatives.*

By William Henry Perkin, jun., and John Lionel Simonsen.

It has long been known that substances containing the *cyclo*propane ring exhibit very remarkable differences in stability, especially towards hydrobromic acid. In some cases, for example in the case of *cyclo*propane-1 : 1-dicarboxylic acid, the ring suffers disruption in contact with hydrobromic acid in the cold :

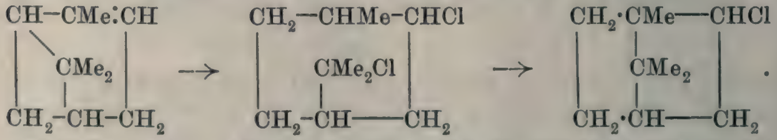

CH_2 / $CH_2\cdot C(CO_2H)_2$ $\longrightarrow$ $CH_2Br\cdot CH_2\cdot CH(CO_2H)_2$,

whereas *cyclo*propane-1 : 2-dicarboxylic acid,


$CH\cdot CO_2H$ / $CH_2\cdot CH\cdot CO_2H$,

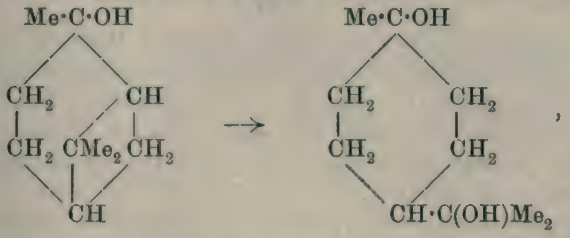
is not affected even when boiled with concentrated aqueous hydrobromic acid. These important differences in stability in the *cyclo*propane series have already been discussed in some detail in previous papers (compare especially Trans., 1894, **65**, 951 ; 1907, **91**, 816), and fresh examples of the instability of the *cyclo*propane ring, especially in such bridged-ring compounds belonging to the terpene series, as carone and sabinene, are constantly being observed.

It is also well known that the *cyclo*butane ring, when it forms part of a bridged-ring complex, not infrequently exhibits marked instability. Thus, in the conversion of pinene into *iso*bornyl chloride by the action of hydrogen chloride at 0°, it is assumed that the dimethyl*cyclo*butane bridged-ring suffers disruption, and rearrangement subsequently takes place according to the scheme :



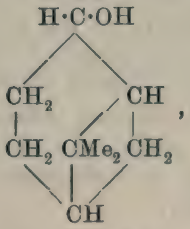
If this representation of the process should prove to be correct, the disruption of the dimethyl*cyclo*butane ring which it involves, together with the subsequent rearrangement, must constitute one of the most remarkable changes in organic chemistry.

That the dimethyl*cyclo*butane ring readily suffers disruption in bridged-ring compounds receives further confirmation from the recent work of Wallach (*Annalen*, 1907, **356**, 241), who has shown that methylnopinol is converted into terpene hydrate by shaking with 5 per



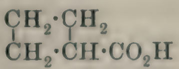
cent. sulphuric acid, or even with dilute oxalic acid, at the ordinary temperature, and further that, when treated with hydrochloric acid, it yields dipentene dihydrochloride.

In view of these facts, it is remarkable that nopinol itself is not



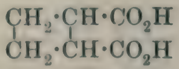
affected by contact with dilute sulphuric acid for four weeks (*loc. cit.*, p. 237). It is very difficult to understand why the substitution of hydrogen for methyl in nopinol should bring about such a marked change in the condition of stability.

If we turn from the consideration of bridged-rings to the study of the stability of the *cyclo*butane ring by itself, such evidence as there is seems to point to that ring being distinctly more stable than the *cyclo*propane ring. Thus *cyclo*butanecarboxylic acid (I) and *cyclo*butane-1 : 2-dicarboxylic acid (II) may be brominated at the temperature of the water-bath under the usual conditions, with formation of bromo*cyclo*butanecarboxylic acid (III) and dibromo*cyclo*butane-1 : 2-dicarboxylic acid (IV):



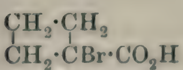
$$\begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CH\cdot CO_2H \end{array}$$

(I.)



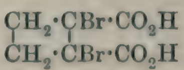
$$\begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ CH_2\cdot CH\cdot CO_2H \end{array}$$

(II.)



$$\begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CBr\cdot CO_2H \end{array}$$

(III.)

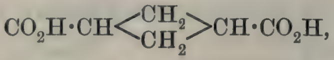


$$\begin{array}{l} CH_2\cdot CBr\cdot CO_2H \\ CH_2\cdot CBr\cdot CO_2H \end{array}$$

(IV.)

and there is no evidence that the hydrogen bromide produced during the bromination caused appreciable fission of the ring in either case.

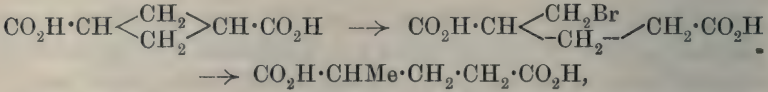
*cyclo*Butane-1 : 3 :-dicarboxylic acid,



$$CO_2H\cdot CH{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}CH\cdot CO_2H,$$

has been synthesised in several ways (compare Haworth and Perkin, Trans., 1898, **73**, 330), but the yields obtained have always been so small that a complete investigation of its properties has, so far, not been attempted. Recently, however, Simonsen (Trans., 1908, **93**, 1778) has worked out a process by which the *cis*-modification may be prepared in quantity, and since it is clear that this acid is more closely allied to the bridged-ring compounds, pinene, nopinol, and methylnopinol, than either of the *cyclo*butanecarboxylic acids just mentioned, we determined to investigate its behaviour with sulphuric acid, hydrobromic acid, and also with bromine.

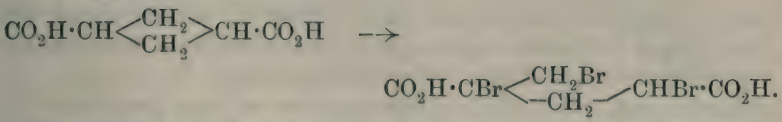
We found, in the first place, that this acid is not affected by boiling with 10 per cent. sulphuric acid, and, even if heated with concentrated sulphuric acid for three hours on the water-bath, very little change takes place, and almost the whole of the acid may be recovered. When, however, the acid is heated in a sealed tube at 100° with fuming hydrobromic acid, the ring suffers disruption, and an almost quantitative yield of a monobromo-acid is obtained, which, since it yields α-methylglutaric acid on reduction, is probably α-bromobutane-$\beta\delta$-dicarboxylic acid :



$$CO_2H\cdot CH{<}\begin{matrix}CH_2\\ CH_2\end{matrix}{>}CH\cdot CO_2H \longrightarrow CO_2H\cdot CH{<}\begin{matrix}CH_2Br\\ -CH_2-\end{matrix}{\diagup}CH_2\cdot CO_2H$$

$$\longrightarrow CO_2H\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO_2H,$$

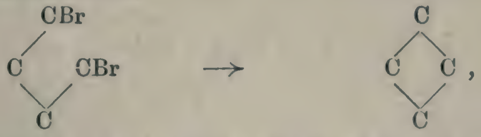
but it is, of course, also possible that the bromo-acid has the constitution $CO_2H\cdot CHMe\cdot CH_2\cdot CHBr\cdot CO_2H$. The readiness with which this disruption of the *cyclo*butane ring takes place led us to investigate the behaviour of *cis*-*cyclo*butane-1 : 2-dicarboxylic acid with hydrogen bromide under the same conditions, but, even after heating at 100° for three hours, no appreciable change could be observed, and almost the whole of the acid was recovered unchanged. Obviously we have here again a case of the remarkable effect on the stability of a closed ring exercised by mere change in position of the substituting groups. We next investigated the action of bromine (2 mols.) on the acid chloride of *cyclo*butane-1 : 3-dicarboxylic acid (1 mol.) at the temperature of the water-bath, and found that the product of the action, after decomposing with water, is a *tribromo-acid*, $C_6H_7O_4Br_3$. This acid has therefore been produced by the substitution of two atoms of hydrogen by bromine in the usual positions, and at the same time the *cyclo*butane ring has suffered disruption owing to the addition of hydrogen bromide produced during the reaction :



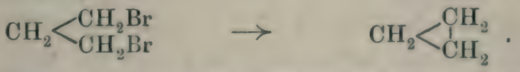
$$CO_2H\cdot CH\Big\langle\begin{matrix}CH_2\\CH_2\end{matrix}\Big\rangle CH\cdot CO_2H \longrightarrow CO_2H\cdot CBr\Big\langle\begin{matrix}CH_2Br\\CH_2\end{matrix}\Big\rangle CHBr\cdot CO_2H.$$

The tribromo-acid is therefore *αβδ-tribromobutane-βδ-dicarboxylic acid.* The most striking property of this acid is the fact that its methyl ester is quantitatively converted into *cyclo*butane-1 : 3-dicarboxylic acid when it is treated with zinc and acetic acid and subsequently hydrolysed, reduction and closing of the ring taking place simultaneously.

It is well known that some αβ-dibromo-acids are readily converted into the corresponding unsaturated acids by the action of zinc; thus, for example, αβ-dibromobutyric ester yields crotonic ester when its ethereal solution is treated with zinc filings (Michael and Schulthess, *J. pr. Chem.*, 1891, [ii], **43**, 590). Assuming Baeyer's "Spannungs Theorie" to be correct, a change of this kind should take place with greater ease in the case of the formation of a *cyclo*butane ring from an αδ-dibromide,



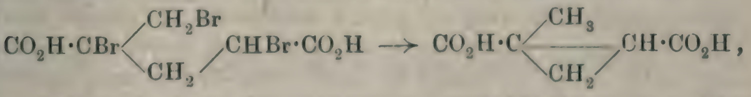
than in the formation of the ethenoid linking, because the "Spannung" in the closed four-carbon ring is much less than that in the ethenoid linking. And the same appears to be true in the *cyclo*propane series, since Gustavson (*Compt. rend.*, 1899, **128**, 437; *J. pr. Chem.*, 1891, [ii], **59**, 302) has shown that *cyclo*propane is almost quantitatively produced when an alcoholic solution of trimethylene bromide is digested with zinc:



$$CH_2\Big\langle\begin{matrix}CH_2Br\\CH_2Br\end{matrix} \longrightarrow CH_2\Big\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}\ .$$

It is therefore to be expected that ring formation will often be found to result from the action of zinc and other metals on αγ-, αδ-, αε-, and possible other more extended dibromo-compounds.

One other point in connexion with the formation of *cyclo*butane-1 : 3-dicarboxylic acid by the elimination of bromine from αβδ-tribromobutane-βδ-tricarboxylic acid is of interest. This elimination might result in the formation of a methyl*cyclo*propanedicarboxylic acid:

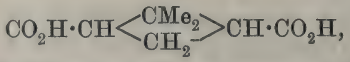


$$CO_2H\cdot CBr\Big\langle\begin{matrix}CH_2Br\\CH_2\end{matrix}\Big\rangle CHBr\cdot CO_2H \longrightarrow CO_2H\cdot C\Big\langle\begin{matrix}CH_3\\ \text{———}\\CH_2\end{matrix}\Big\rangle CH\cdot CO_2H,$$

especially as the two α-bromo-atoms are probably the most reactive, and the fact that the reaction actually proceeds quantitatively with formation of the *cyclo*butane ring is additional evidence that this ring is more readily formed than the *cyclo*propane ring.

During the course of this investigation we have prepared large quantities of pinonic acid, and have made several new observations in connexion with this acid and its derivatives. The results of these experiments are described on p. 1174, and it will be only necessary, in this introduction, to discuss the experiments which illustrate the extraordinary stability of norpinic acid.

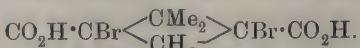
Norpinic acid,



$$\mathrm{CO_2H{\cdot}CH}<\substack{\mathrm{CMe_2}\\ \mathrm{CH_2}}>\mathrm{CH{\cdot}CO_2H},$$

is the *gem*-dimethyl derivative of *cyclo*butane-1 : 3-dicarboxylic acid, and, like this acid, it exists in *cis*- and *trans*-modifications.

Its investigation was thought to be interesting because this acid is a simple derivative of that dimethyl*cyclo*butane ring which, as has already been pointed out (p. 1166), so readily undergoes disruption when it is a constituent of the bridged-ring characteristic of pinene, nopinone, etc. Our experiments have, however, shown that this ring, in norpinic acid, exhibits quite unusual stability, and it is quite clear, therefore, that the closing of the bridged-ring in compounds such as pinene entirely alters the character of the dimethyl*cyclo*butane ring, possibly by producing a "strain" which is not present in the ring itself. Although *cis-cyclo*butane-1 : 3-dicarboxylic acid readily undergoes fission when it is treated with hydrobromic acid at 100°, this reagent has no action on *cis*-norpinic acid at 120°. Again, it is pointed out on p. 1168 that *cis-cyclo*butane-1 : 3-dicarboxylic acid is readily attacked by bromine at 100° with disruption of the ring and formation of $\alpha\beta\delta$-tribromobutane-$\beta\delta$-dicarboxylic acid. Baeyer (*Ber.*, 1896, **29**, 1911) states that the *cis*-norpinic acid yields a bromo-acid when it is treated with bromine by the Volhard method, and we can confirm this, but our experiments show that the acid chloride is attacked only with great difficulty by bromine at 100°, and that at 120° a bromo-acid is produced which, although not obtained pure, is doubtless 1 : 3-*dibromo*-cis-*norpinic acid*,



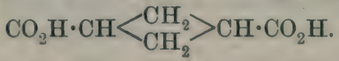
$$\mathrm{CO_2H{\cdot}CBr}<\substack{\mathrm{CMe_2}\\ \mathrm{CH_2}}>\mathrm{CBr{\cdot}CO_2H}.$$

In this case, also, there is no evidence of any fission of the closed ring. It has already been pointed out (p. 1167) that the dimethyl*cyclo*butane ring in certain derivatives of pinene readily suffers disruption under the influence of weak acids, but norpinic acid, on the other hand, may be boiled with 10 per cent. sulphuric acid or heated on the water-bath with concentrated sulphuric acid without change.

Results such as the above clearly show (*a*) that comparatively slight changes, such as the introduction of methyl groups or the rearrangement of carboxyl groups, exercise a great influence on the stability of the *cyclo*butane ring, and (*b*) that this ring undergoes a remarkable reduction in stability when it becomes part of a bridged-ring system.

EXPERIMENTAL.

cis-cyclo*Butane*-1 : 3-*dicarboxylic Acid*,



$$CO_2H\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CO_2H.$$

We have succeeded in devising two new methods for the preparation of this acid.

I. *By Condensation of Monochloromethyl Ether with the Sodium Derivative of Ethyl Methylenedimalonate.*

Ethyl methylenedimalonate (35 grams) was added to finely divided sodium (2·5 grams) suspended in dry ether, when a vigorous reaction ensued, and, after remaining overnight, the sodium had completely dissolved and a yellow sodium derivative separated. Monochloromethyl ether (10 grams), dissolved in an equal volume of dry ether, was then added all at once, and in two hours the reaction, which proceeds without the evolution of much heat, was complete and much sodium chloride had separated. The product was mixed with water, the ethereal solution separated, dried, and evaporated, when a colourless oil remained which, after several fractionations, distilled fairly constantly at 215—220°/24 mm.:

0·1226 gave 0·2413 CO_2 and 0·08 H_2O. $C=53\cdot7$; $H=7\cdot2$.

$C_{17}H_{28}O_9$ requires $C=54\cdot2$; $H=7\cdot4$ per cent.

This oil undoubtedly consists of ethyl δ-methoxybutane-*ααγγ*-tetracarboxylate, a substance which had already been obtained by a quite different process (Trans., 1908, **93**, 1784). This ester (3 grams) was mixed with 50 per cent. hydrochloric acid (25 c.c.) and digested on the sand-bath in a reflux apparatus for twelve hours, when hydrolysis was complete. On removing the excess of hydrochloric acid by evaporation, an oil was obtained which rapidly solidified, and after two crystallisations from dry ether, the acid melted at 129° and was found on examination to consist of *cis-cyclo*butane-1 : 3-dicarboxylic acid.

II. *By the Condensation of Ethyl Methylenedimalonate with Methylal.*

In carrying out this interesting condensation, the following method was, after several comparative experiments, found to give the best results. Ethyl methylenedimalonate (20 grams) was mixed with methylal (30 grams) and zinc chloride (0·5 gram) and heated in a sealed tube for two hours at 150—160° and then for one hour at 170°, and during the operation the tube was occasionally agitated in order to keep the contents well mixed. After cooling, the pale brown solution was poured into water, the oil which separated dissolved in ether, the ether was then evaporated, and the residual oil fractionated under diminished pressure, when a considerable quantity (9 grams) distilled at 200—220°/20 mm., a small, high boiling residue remaining in the flask. This crude oil, without further purification, was hydrolysed by boiling with 50 per cent. hydrochloric acid, when, after removing the hydrochloric acid by evaporation, a brown oil was obtained which soon almost completely solidified. After draining on porous porcelain, the acid was crystallised from ether, and found to melt at 128—130° and consist of pure *cis-cyclo*butane-1 : 3-dicarboxylic acid :

0·1346 gave 0·2456 CO_2 and 0·0642 H_2O. $C = 49·8$; $H = 5·3$.

$C_6H_8O_4$ requires $C = 50·0$; $H = 5·6$ per cent.

The *anhydride* of cis-cyclo*butane*-1 : 3-*dicarboxylic acid.*—As we were desirous, in our further experiments, to employ the pure *cis*-acid quite free from even traces of the *trans*-isomeride, we decided to purify it by conversion into the anhydride. The anhydride was obtained by digesting the acid with acetyl chloride in the manner previously described (Trans., 1898, **73**, 338), but, on the present occasion, it was purified by distillation under diminished pressure, when it was found to boil at 175—177°/20 mm. as a colourless oil which soon solidified, and, after remaining in contact with porous porcelain, the crystalline mass melted at 50—51°. The pure *cis*-acid, obtained from the anhydride by hydrolysis, melted sharply at 135—136°.

Bromination of cis-cyclo*Butane*-1 : 3-*dicarboxylic Acid.* *Formation of* $\alpha\beta\delta$-*Tribromobutane*-$\beta\delta$-*dicarboxylic Acid,*

$CH_2Br\cdot CBr(CO_2H)\cdot CH_2\cdot CHBr\cdot CO_2H$.

The pure acid (2 grams) was digested with phosphorus pentachloride (5·8 grams) until decomposition was complete, and then heated with bromine (4·6 grams) in a sealed tube in a boiling-water bath for fifteen hours. The bromo-acid chloride was left in contact with powdered ice for two days, the heavy, viscid syrup extracted with ether, the ethereal solution well washed, dried, and evaporated, when an almost colourless syrup remained which rapidly crystallised. After remaining in contact with porous porcelain until quite dry, the solid residue was several times recrystallised from ether :

0·1184 gave 0·1726 AgBr. Br = 62·0.

$C_6H_7O_4Br_3$ requires Br = 62·7 per cent.

αβδ-Tribromobutane-βδ-dicarboxylic acid separates from ether in crusts of small plates, and melts with decomposition at 172°.

It is readily soluble in ether, formic acid, or hot water, but only sparingly so in benzene, chloroform, or light petroleum.

Methyl αβδ-Tribromobutane-βδ-dicarboxylate.—This substance was obtained by pouring the bromo-acid chloride, prepared as described above, into well cooled methyl alcohol. After remaining overnight, the methyl ester was precipitated by water, the heavy oil extracted with ether, the ethereal solution washed well with water and sodium carbonate, dried, evaporated, and the pale yellow oil left for some days in a vacuum desiccator over sulphuric acid. Two different preparations gave the following results on analysis:

0·1453 gave 0·1939 AgBr. Br = 56·8.
0·1681 „ 0·2261 AgBr. Br = 57·3.

$C_8H_{11}O_4Br_3$ requires Br = 58·4 per cent.

As it seemed possible that the remarkable course of the bromination of *cis-cyclo*butane-1 : 3-dicarboxylic acid was due to the pressure of the hydrogen bromide in the sealed tube, an experiment was made with the same quantities as before, but in an open flask fitted with a ground-in tube. The bromination proceeded on the water-bath very slowly, and, as soon as it was complete, the product was poured into methyl alcohol as described above. On analysis, the methyl ester was found to have practically the same composition as before:

0·2089 gave 0·2720 AgBr. Br = 55·4.

$C_8H_{11}O_4Br_3$ requires Br = 58·4 per cent.

Reduction of Methyl αβδ-Tribromobutane-βδ-tricarboxylate to cis cyclo*Butane*-1 : 3-*dicarboxylic acid.*—The bromo-methyl ester (4 grams), dissolved in acetic acid and a little water, was treated with zinc dust (20 grams), at first in the cold and afterwards on the water-bath. After filtering from undissolved zinc, water was added, the oil extracted with ether, and the ethereal solution well washed and evaporated.

The residual oil, which was quite free from bromine, was then hydrolysed with alcoholic potash, the solution mixed with water, evaporated until free from alcohol, acidified, and extracted several times with ether. After removing the ether by evaporation, a solid was obtained which separated from water in prisms melting at 131—133°, and consisted of *cis-cyclo*butane-1 : 3-dicarboxylic acid, the yield being nearly quantitative:

0·1682 gave 0·3081 CO_2 and 0·0831 H_2O. C = 49·9 ; H = 5·5

$C_6H_8O_4$ requires C = 50·0 ; H = 5·6 per cent.

Action of Hydrogen Bromide on cis-cyclo*Butane*-1 : 3-*dicarboxylic Acid. Formation of* α-*Bromobutane*-βδ-*dicarboxylic Acid.*

In order to determine whether fission of the ring took place when *cis-cyclo*butane-1 : 3-dicarboxylic acid was heated with hydrobromic acid alone, the pure acid (1 gram) was mixed with aqueous hydrobromic acid (saturated at 0°, 10 c.c.) and heated in a sealed tube at 100° for three hours. The hydrobromic acid was then removed on the water-bath, when an oil remained which completely solidified, and, after crystallisation from benzene, the following results were obtained on analysis:

0·1113 gave 0·0922 AgBr. Br = 35·2.

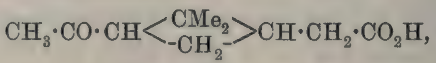
$C_6H_9O_4Br$ requires Br = 35·5 per cent.

α-Bromobutane-βδ-dicarboxylic acid, which does not appear to have been previously described, separates from benzene, in which it is fairly readily soluble, in hard, nodular clusters of needles and melts at 106—107°. It is readily soluble in ether, water, or formic acid, but sparingly so in chloroform or light petroleum.

Reduction to α-Methylglutaric Acid.—This reduction, which proves the constitution of the bromo-acid, was carried out by treating the acid, dissolved in dilute sodium carbonate, with a large excess of sodium amalgam in the cold. The solution was acidified, extracted several times with pure ether, the ether evaporated, and the solid residue left in contact with porous porcelain until quite dry and then crystallised from ether:

0·1135 gave 0·2045 CO_2 and 0·0731 H_2O. C = 49·1 ; H = 7·1.

$C_6H_{10}O_4$ requires C = 49·3 ; H = 6·9 per cent.



Pinonic Acid, $CH_3\cdot CO\cdot CH<^{CMe_2}_{-CH_2-}>CH\cdot CH_2\cdot CO_2H$, *and its Derivatives.*

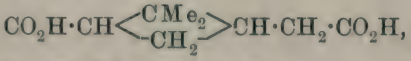
The large quantities of pinonic acid which have been prepared for the present investigation and during the course of our experiments on nopinone (Trans., 1907, **91**, 1736) were obtained by the oxidation of pinene under the conditions recommended by Baeyer (*Ber.*, 1896, **29**, 22). In purifying crude pinonic acid, we have found it advantageous, instead of distilling the acid itself as recommended by Baeyer, to convert it into its ester by digesting with alcohol and sulphuric acid, and then to fractionate this carefully under diminished pressure. The fraction distilling at 147—148°/16 mm. is pure *ethyl pinonate*, as the following analysis shows:

0·1141 gave 0·2858 CO_2 and 0·0975 H_2O. C = 68·2 ; H = 9·5.

$C_{12}H_{20}O_3$ requires C = 68·0 ; H = 9·4 per cent.

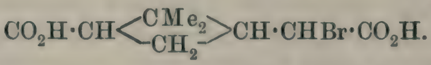
When this ester is hydrolysed, it yields a syrup which soon becomes semi-solid, and doubtless consists of the *cis*- and *trans*-modifications of pinonic acid. In contact with porous porcelain, the syrup is absorbed, and the crystalline residue separates from water in colourless prisms melting at 103—105°.

In preparing *cis*-pinic acid,



$$CO_2H\cdot CH<\begin{matrix}CMe_2\\CH_2\end{matrix}>CH\cdot CH_2\cdot CO_2H,$$

by the method described by Baeyer (*loc. cit.*, p. 25), we have also found that it is best purified by conversion into the ester, which distils at 156°/20 mm., and, on hydrolysis, at once yields the pure acid.



cis-*Bromopinic Acid*, $CO_2H\cdot CH<\begin{matrix}CMe_2\\CH_2\end{matrix}>CH\cdot CHBr\cdot CO_2H$.

Baeyer (*loc. cit.*, p. 1908) prepared this acid in a crude condition by the action of phosphorus tribromide and bromine on *cis*-pinic acid, but did not purify it. We have found that the pure bromo-acid is readily obtained by the following modification of Baeyer's process.

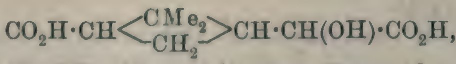
Pure *cis*-pinic acid (43 grams) is mixed with phosphorus pentachloride (100 grams), and, as soon as the vigorous action has subsided, the mixture is heated on the water-bath for half an hour. Bromine (13 grams) is then added to the well-cooled acid chloride, and the whole heated on the water-bath for three hours, care being taken so to regulate the process that there is no loss of bromine.

The product is poured in a thin stream into excess of anhydrous formic acid, and the solution heated on the water-bath until decomposition is complete, when, on keeping in the ice-chest, a quantity of a crystalline acid separates, which is collected and recrystallised from formic acid:

0·124 gave 0·0900 AgBr. Br = 30·9.

$C_9H_{13}O_4Br$ requires Br = 30·2 per cent.

cis-*Bromopinic acid* melts at about 154°, and separates from formic acid, in which it is sparingly soluble in the cold, in nodular masses composed of stout plates.

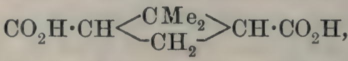


cis-*Hydroxypinic acid*, $CO_2H\cdot CH<\begin{matrix}CMe_2\\CH_2\end{matrix}>CH\cdot CH(OH)\cdot CO_2H$, is conveniently prepared in the following way (compare Baeyer, *loc. cit.*, p. 1908). The bromo-acid chloride, obtained as explained above, is left in contact with ice until decomposed, and the syrup extracted with ether. After removing the ether by evaporation, the residue is digested with excess of barium hydroxide for one hour, the alkaline liquid filtered from tarry matter, concentrated, acidified, and extracted five times with ether. The ethereal solution yields, on concentration, a crystalline mass of pure *cis*-hydroxypinic acid, melting at 191—193°.

Ethyl cis-*hydroxypinate* is readily obtained by treating the acid with alcoholic sulphuric acid in the usual manner. It distils at 179°/16 mm. as a colourless oil, which rapidly crystallises, and separates from light petroleum in colourless needles melting at 58—60°:

0·1729 gave 0·3821 CO_2 and 0·1335 H_2O. C = 60·3; H = 8·6.

$C_{13}H_{22}O_5$ requires C = 60·5; H = 8·5 per cent.

cis-Norpinic acid,  $CO_2H\cdot CH\Big<\begin{matrix}CMe_2\\CH_2\end{matrix}\Big>CH\cdot CO_2H$, is obtained, as Baeyer (*loc. cit.*, p. 1910) has shown, by the oxidation of hydroxypinic acid with chromic acid. We have prepared large quantities of this acid, and, during the course of our experiments, have obtained several derivatives which do not appear to have been previously described.

Ethyl cis-*norpinate* is readily obtained by treating the acid with alcohol and sulphuric acid in the usual manner, and is a colourless, mobile oil with a pleasant ethereal odour, which distils at 140°/20 mm.:

0·1223 gave 0·2826 CO_2 and 0·0951 H_2O. C = 63·0; H = 8·6.

$C_{12}H_{20}O_4$ requires C = 63·2; H = 8·8 per cent.

cis-*Norpinic anhydride* was prepared by heating the acid with excess of acetic anhydride in a sealed tube at 220°. The excess of acetic anhydride was removed under the ordinary pressure, and the residue rapidly distilled under 10 mm. pressure, when a syrup was obtained which soon crystallised. After remaining in contact with porous porcelain until quite dry, the anhydride was recrystallised from ether:

0·1539 gave 0·3474 CO_2 and 0·0898 H_2O. C = 62·2; H = 6·5.

$C_8H_{10}O_3$ requires C = 62·3; H = 6·5 per cent.

cis-*Norpinic anhydride* separates from ether in slender plates, melts at 135°, and, when warmed with water, is slowly converted into the crystalline acid, which melts at 173—175°, and is identical with the acid which is directly obtained by the oxidation of hydroxypinic acid.

It is clear, therefore, that norpinic acid and hydroxypinic acid, and probably also pinic acid and pinonic acid, belong to the *cis*-series.

trans-*Norpinic Acid.*—This acid, which does not appear to have been previously described, is obtained when the *cis*-acid is heated either with hydrochloric or with hydrobromic acid. The pure *cis*-acid (5 grams) is heated with hydrochloric acid (15 c.c.) and water (5 c.c.) in a sealed tube at 180° for two hours. The product is heated on the water-bath until free from hydrochloric acid, and the solid residue, which consists of a mixture of the *cis*- and *trans*-acids, is fractionally crystallised from ether until nearly all of the less soluble *cis*-acid has been removed, and then from hydrochloric acid; from this solvent the pure *trans*-acid is ultimately obtained in hard nodules, which, under the microscope, are seen to be composed of slender prisms:

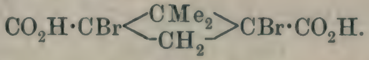
0·1106 gave 0·2265 CO_2 and 0·0725 H_2O. C = 55·8; H = 7·3.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

trans-*Norpinic acid* softens at 137°, melts at 144°, and is more soluble in the usual solvents than the *cis*-modification.

Bromination of cis-*Norpinic Acid.*

cis-Norpinic acid is brominated with much greater difficulty than *cis-cyclo*butane-1 : 3-dicarboxylic acid, and evidently with the formation of 1 : 3-*dibromonorpinic acid*,



$$CO_2H\cdot CBr<\begin{matrix}CMe_2\\ CH_2\end{matrix}>CBr\cdot CO_2H.$$

Norpinic acid (2 grams) was mixed with phosphorus pentachloride (5 grams), and, after the reaction had subsided, the mixture was heated on the water-bath for half an hour. Bromine (3·7 grams) was then added, and the whole heated in a sealed tube for forty-eight hours in a boiling-water bath, but, as the action was then not nearly complete, the heating was continued for three hours at 120°, when almost the whole of the bromine had disappeared. The bromo-acid chloride was decomposed by ice, the viscid, brown syrup dissolved in ether, and the ethereal solution dried and evaporated. The syrup, which showed no tendency to crystallise, was placed in a vacuum desiccator over sulphuric acid for some days and then analysed:

0·2515 gave 0·2500 AgBr. Br = 42·3.

$C_8H_{10}O_4Br_2$ requires Br = 48·5 per cent.

Although this result, as was to be expected, is only approximate, it clearly indicated that the product of the action of bromine on norpinic acid, under the conditions employed, is 1 : 3-dibromonorpinic acid, and this receives support from the fact that the bromo-acid yields norpinic acid when it is reduced by sodium amalgam in sodium carbonate solution. In confirmation of the above result, a second experiment was made in which the bromo-acid chloride was poured into methyl alcohol, when the methyl ester, extracted in the usual manner, was found to be a pale yellow oil, possessing a pungent odour, and having an unpleasant effect on the eyes:

0·1659 gave 0·1524 AgBr. Br = 39·1.

$C_{10}H_{14}O_4Br_2$ requires Br = 44·7 per cent.

This result again emphasises the difference in behaviour of *cyclo*butane-1 : 3-dicarboxylic acid and norpinic acid on bromination (p. 1172).

We wish to thank Messrs. G. S. Naylor and H. D. Gardner for assisting us in the preparation of the large quantities of pinonic acid required for these experiments, and our thanks are also due to the Research Fund Committee of the Chemical Society for a Grant, which has defrayed much of the expense of this investigation.

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CXXXII.—*Sodium Sulphite and its Equilibrium with Water.**

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN the course of an investigation of the products of crystallisation of mixed solutions of sodium and potassium sulphites, it was found necessary to determine the properties of the end members of the series as little information was available concerning them.

Sodium sulphite has been studied previously by Fourcroy (Comey, *Dictionary of Solubilities*, 1896, p. 464), Mitscherlich (*Pogg. Annalen*, 1827, **12**, 140), Rammelsberg (*Pogg. Annalen*, 1846, **67**, 246; 1855, **94**, 507), Muspratt (*Phil. Mag.*, 1847, [iii], **30**, 414), Marignac (*Ann. des Mines*, 1857, [v], **12**, 32), Kremers (*Pogg. Annalen*, 1856, **99**, 50), Des Cloizeaux (*Ann. des Mines*, 1857, [v], **11**, 347; 1858, [v], **14**, 391), Schultz-Sellack (*J. pr. Chem.*, 1870, [ii], **2**, 459), de Forcrand (*Ann. Chim. Phys.*, 1884, [vi], **3**, 243), Röhrig (*J. pr. Chem.*, 1888, [ii], **37**, 222), Hartog (*Compt. rend.*, 1889, **109**, 179, 221, 436), Traube (*Zeitsch. Kryst. Min.*, 1894, **22**, 143), and Barth (*Zeitsch. physikal. Chem.*, 1892, **9**, 176).

Three forms have been described by one or other of the above authors, namely, Na_2SO_3, $Na_2SO_3,7H_2O$, and $Na_2SO_3,10H_2O$. Of these the heptahydrate is stable at low temperatures, and the anhydrous salt at high. The decahydrate, first described by Muspratt, is a labile modification; its existence has been questioned by Schultz-Sellack and Röhrig, and we have failed to isolate it in spite of a large number of attempts under different conditions; however, the formation of mixed crystals of $Na_2CO_3,10H_2O$ and $Na_2SO_3,10H_2O$, observed by Traube

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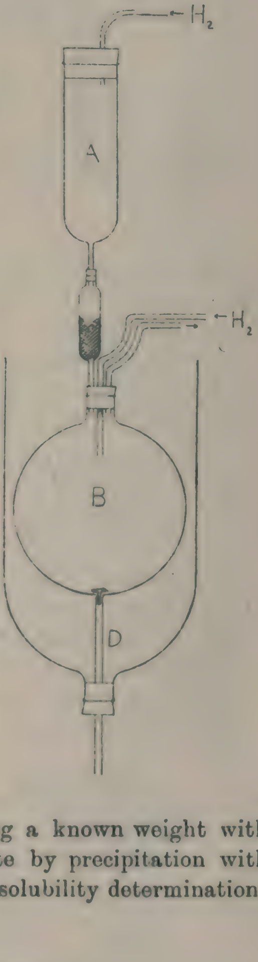
* This title is substituted for that given in the abstract (Proc., 1909, **25**, 164).

(*loc. cit.*), makes it probable that the decahydrate might crystallise under exceptional circumstances. The present paper deals with the preparation of pure sodium sulphite, the properties of the anhydrous salt, the solubility of sodium sulphite in water, and the spontaneous crystallisation of its supersaturated solutions.

Preparation of Materials.

FIG. 1.



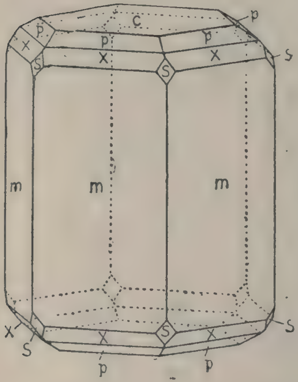
As the hydrated salt oxidises very readily in air, whilst the anhydrous modification is stable so long as it is kept dry, a quantity of pure anhydrous salt was prepared for use in the determinations. For this purpose, 40 grams of Merck's pure sodium carbonate were dissolved in 120 grams of air-free water, and a current of sulphur dioxide passed into the solution until the gain in weight showed that it was converted into sodium hydrogen sulphite; an equal quantity of sodium carbonate solution was then added, and the solution was quickly transferred to the vessel, *A* (Fig. 1), containing hydrogen, whence it was filtered through glass wool into the vessel *B*, which was surrounded by a bath of brine kept at a temperature of over 100° by blowing in steam. As the anhydrous salt is less soluble than the hydrated form above 22°, it crystallises when the temperature of the solution is raised, and the yield is increased by evaporating the solution in a stream of hydrogen. After some hours, the solution was drawn off by the tube *D*, the crystals being stopped by a small glass plug. The crystals were first washed with a mixture of alcohol and water, then with alcohol, and finally dried, all the operations being carried on in an atmosphere of hydrogen. The yield varied from 11 to 24 grams. The salt prepared by this method was free from sulphate. It was analysed by oxidising a known weight with bromine water and determining the sulphate by precipitation with barium chloride. The specimen used in the solubility determinations gave the following results:

0·6674 gave 1·2334 $BaSO_4$. $SO_3 = 63·34$.

Na_2SO_3 requires $SO_3 = 63·47$ per cent.

The salt therefore contained 99·87 per cent. of pure sodium sulphite. The results of two other analyses gave $SO_3 = 63{\cdot}23$ and 63·37 respectively. For experiments where the hydrated salt was required, a specimen recrystallised in hydrogen was used, but this never contained less than one per cent. of sulphate as an impurity.

FIG. 2.



Crystalline Form.

The crystalline form of hydrated sodium sulphite has been investigated by Rammelsberg (*loc. cit.*), Marignac (*loc. cit.*), and Des Cloizeaux (*loc. cit.*), who showed it to belong to the prismatic class of the monoclinic system with the axial ratios:

$$a : b : c = 1{\cdot}5728 : 1 : 1{\cdot}1694\ ;\ \beta = 93°36'.$$

The anhydrous salt had not been investigated before. It crystallises in short, hexagonal prisms terminated by a basal plane and pyramid faces as shown in Fig. 2. The crystals were small, and the faces gave poor reflections.

System: Hexagonal (probably holohedral).

Axial ratios: $a : c = 1 : 1{\cdot}1246$.

Forms observed: $c\{0001\}$, $m\{10\bar{1}0\}$, $x\{10\bar{1}1\}$, $p\{10\bar{1}2\}$, $s\{11\bar{2}1\}$.

Angle measured.	Readings.	Limits.	Mean.	Calculated.
$c : x = 0001 : 10\bar{1}1$	13	52°36′—52° 4′	52°24′	—
$c : p = 0001 : 10\bar{1}2$	6	32 54 —31 48	32 16	32°59′
$c : s = 0001 : 11\bar{2}1$	6	66 30 —65 0	65 40	66 2

The crystals possess a perfect cleavage parallel to the basal plane, they are strongly birefringent, cleavage fragments showing a uniaxial figure of negative character in convergent light.

The densities of both hydrated and anhydrous crystals were determined by the method of flotation in a mixture of xylene and acetylene tetrabromide with the following results:

$Na_2SO_3,7H_2O$.		Na_2SO_3.	
Temperature of observation.	Δ_4^{15}.	Temperature of observation.	Δ_4^{15}.
15·2°	1·5934	15·4°	2·6327
15·2	1·5944	15·0	2·6352
15·2	1·5944	15·4	2·6319
14·8	1·5934	15·4	2·6336
13·8	1·5945	15·4	2·6341
Mean......	1·5939	Mean......	2·6334

Buignet (*J. Pharm.*, 1861, [iii], **40**, 161, 337) gives a value for the specific gravity of the hydrated salt of 1·561.

Solubility Relations.

Freezing Points.—The freezing points of dilute solutions of sodium sulphite were found by the ordinary Beckmann method, the determinations being carried out in an atmosphere of hydrogen. The results are given in the following table, and are plotted in Fig. 3. The salt was added in the anhydrous condition, and owing to the sluggish transformation of the anhydrous salt into the less soluble hydrated modification, it was possible to prolong the freezing-point curve into the metastable region.

Na_2SO_3 in grams.	Water in grams.	Parts of Na_2SO_3 per 100 of water.	Temperature.
0·6888	32·3310	2·15	−0·76°
1·3623	32·3310	4·21	1·37
2·0330	32·3310	6·29	1·96
3·0350	32·3310	9·44	2·77
4 0355	32·3310	12·48	3·51
2·2980	13·3786	17·91	4 50

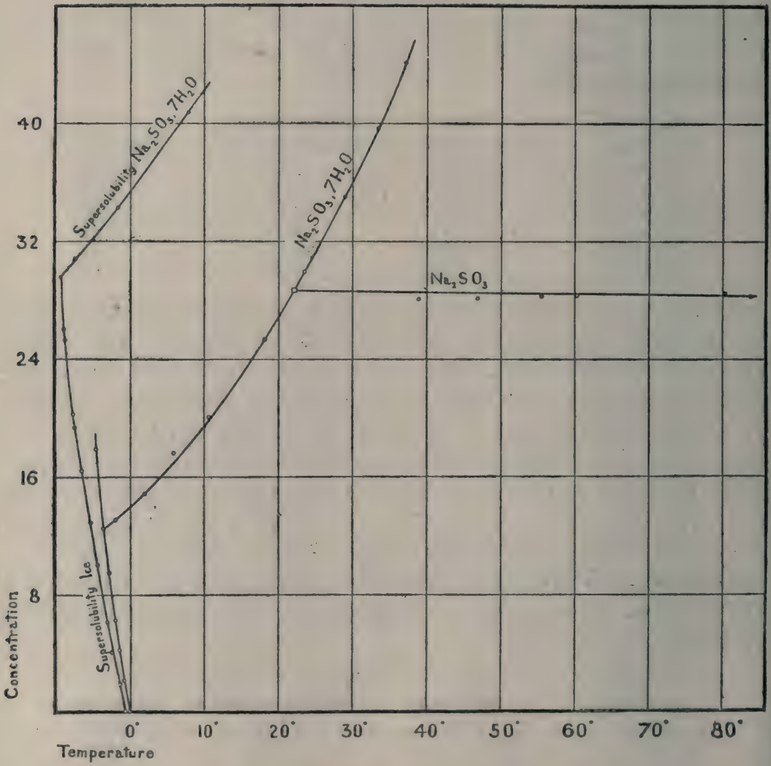
$Na_2SO_3,7H_2O$.—The solubility of the hydrated salt was determined by the sealed tube method, as described by Hartley and Thomas (Trans., 1906, **89**, 1016). Weighed amounts of salt and water were sealed up in small tubes, and two temperatures were found differing by about 0·4°, at the higher of which one or two small crystals were seen to dissolve, and at the lower to grow. The mean of these temperatures was taken as that of equilibrium of a solution of this concentration with the solid phase. The method gave satisfactory results, owing to the steep slope of the solubility curve, and was particularly convenient, as it avoided all difficulties arising from the oxidation of the solution. The results are given in the following table, and are plotted in Fig. 3.

Na_2SO_3 in grams.	Water in grams.	Parts of Na_2SO_3 per 100 parts of water.	Temperature.
0·4519	1·0252	44·08	37·2°
0·4270	1·0772	39·64	33·5
0·4394	1·2557	34·99	29·0
0·2991	0·9997	29·92	23·5
0·3258	1·2870	25·31	18·2
0·2423	1·2970	20·01	10·6
0·1300	0·7379	17·61	5·9
0·2626	1·7723	14·82	2·0
0·1440	1·1000	13·09	−1·9

It will be seen that the solubility curve cuts the ice curve at −3·5°, this being the cryohydric temperature.

Anhydrous Salt.—The tube method could not be used in this case owing to the small temperature-coefficient of the solubility and the slowness with which equilibrium is attained. Excess of the anhydrous salt was therefore stirred with water in a bottle containing hydrogen, air being excluded as far as possible by mercury traps. Portions of the solution were withdrawn and analysed from time to time. In the earlier determinations a weighed amount of solution was oxidised by means of bromine water, and the sulphite determined as sulphate. By this method the true solubility was increased by any sulphate formed by leakage of air into the solubility bottle, and the results were found to be untrustworthy.

FIG. 3.



In order to obtain a direct estimation of the sulphite, a portion of the solution was drawn off through a glass wool filter into a weighed flask containing a known quantity of iodine solution, the flask was again weighed, and the excess of iodine determined by means of standard thiosulphate. Giles and Shearer (*J. Soc. Chem. Ind.*, 1884, 3, 187) have shown that under these conditions oxidation takes place according to the equation:

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI,$$

(compare also Volhard, *Annalen*, 1887, **242**, 94).

The results of two series of experiments are given in the following table:

Time stirred in hours.	Iodine solution in grams.	Na_2SO_3 solution in grams.	Excess of iodine solution in grams.	Parts of Na_2SO_3 per 100 of water.	Temperature.
		Series I.			
11	99·81	5·933	28·56	28·29	60·4°
13	102·64	6·543	22·69	28·89	59·8
25	107·84	6·349	30·83	28·65	59·8
27	104·56	6·424	26·37	28·75	59·8
		Series II.			
96	110·09	9·479	24·53	28·01	37·0
96	109·48	10·800	11·87	28·07	37·0
48	108·71	9·993	17·92	28·19	47·0
100	108·33	10·960	9·27	28·07	47·0
19	110·69	9·242	26·82	28·21	55·6
7	111·04	9·934	20·76	28·26	84·0

These numbers indicate that the solubility of the anhydrous salt is almost independent of the temperature, and that the transition point of the two modifications lies in the neighbourhood of 21·6°. This point was determined independently by means of a dilatometer. The volume of one gram-molecule of the hydrated salt is 158 c.c., while the volume occupied by the same weight of anhydrous salt and water is 178 c.c., the decomposition of the hydrated salt being thus accompanied by an increase of volume. A finely powdered mixture of anhydrous and hydrated salts was placed in the bulb of a dilatometer, which was then sealed off and filled with turpentine. It was placed in a thermostat with an electric regulator, and the readings of the level of the turpentine in the neighbourhood of the transition point were as follows:

Bath temp. = 21·89°.		Bath temp. = 22·09°.		Bath temp. = 22·69°.	
Hours in bath.	Scale reading.	Hours in bath.	Scale reading.	Hours in bath.	Scale reading.
0	146·6	0	146·1	0	145·7
5	145·4	1	146·1	3	145·8
6	145·3	6	146·1	18	146·5
8	145·2	9	146·1	20	146·6
20	144·5	20	146·1	23	146·9

These numbers indicate a transition temperature in the neighbourhood of 22·1°. The transition is extremely sluggish, less than 0·1 per cent.

of the hydrated salt being transformed to the anhydrous variety in twenty hours, when it is 0·6° above the transition temperature. The agreement between the transition temperatures determined by these two methods (21·6° and 22·1°) is as close as was expected in view of the difficulty of determining the solubility of the anhydrous salt.

Spontaneous Crystallisation of Supersaturated Solutions.

The conditions under which ice and salt separate spontaneously from supersaturated solutions of sodium sulphite were investigated in exactly the same manner as in the similar case of sodium sulphate (Hartley, Jones and Hutchinson, Trans., 1907, **93**, 825). Sealed tubes containing solutions freed from crystalline nuclei were cooled down, while they were constantly shaken until crystallisation occurred. One set of experiments was made with tubes containing solid matter and another without, in every case tubes containing solid which produced friction during shaking crystallised at a slightly higher temperature than those which did not. The occurrence of crystallisation was definite in both cases, in spite of the fact that sodium sulphite has the largest metastable region (approximately 30°) that has yet been recorded for a salt solution.

The results are given in the following tables, and the supersolubility curves in presence of solid matter are plotted with the solubility curves in Fig. 3. A comparison of the numbers in the two tables will show that the supersolubility curves in the absence of solid matter lie just outside those drawn in the figure.

Tubes Containing only Solution.

Na_2SO_3 in grams.	Water in grams.	Parts of Na_2SO_3 per 100 parts of water.	Temperature at which spontaneous crystallisation occurred.
0·4519	1·0252	44·08	10·6 S.
0·4270	1·0772	39·84	4·3 S.
0·3977	1·0790	36·86	−0·1 S.
0·4394	1·2557	34·99	−3·1 S.
0·4325	1·2215	34·67	−3·5 S.
0·2991	0·9997	29·92	−10·55 S.
0·3528	1·2870	25·32	−9·7 I.
0·2423	1·2070	20·02	−8·05 I.
0·2626	1·7723	14·82	−6·15 I.
0·2315	2·3380	9·92	−4·5 I.
0·1025	2·0325	5·04	−2·8 I.

Tubes with Solid Matter.

Na_2SO_3 in grams.	Water in grams.		Parts of $NaSO_3$ per 100 parts of water.	Temperature at which spontaneous crystallisation occurred.	
0·2393	0·5870	Glass	40·75	7·9	S.
0·2360	0·6884	,,	34·28	−1·6	S.
0·1698	0·5516	,,	30·80	−7·3	S.
0·8197	2·7750	Garnets	29·54	−9·2	IS.
0·2187	0·8407	Glass	26·01	−8·9	I.
0·6393	2·5317	,,	25·25	−8·7	I.
0·4770	2·3674	Garnets	20·15	−7·6	I.
0·2735	1·1414	,,	19·34	−7·4	I.
0·1322	0·8943	Glass	16·43	−6·4	I.
0·1911	1·4778	,,	12·93	−5·2	I.
0·1664	1·6623	,,	10·00	−4·3	I.
0·1178	1·9381	,,	6·10	−3·0	I.
0·0569	1·4204	,,	4·06	−2·4	I.
0·0426	2·2516	,,	1·89	−1·3	I.

S indicates that $Na_2SO_3,7H_2O$ was produced.
I ,, ,, ice ,, ,,

In one case indicated by IS both phases were observed, this being the hypertectic point.

Water was found to crystallise at −1·0° in absence of solid, and at −0·6° when shaken with fragments of glass.

In no case was there any evidence of the spontaneous crystallisation of a hydrate other than $Na_2SO_3,7H_2O$.

Summary.

1. Sodium sulphite exists in two stable modifications, $Na_2SO_3,7H_2O$ and Na_2SO_3, with a transition point in the neighbourhood of 22°.

2. The hydrated salt crystallises in the monoclinic system, the anhydrous in the hexagonal system.

3. Solubility curves have been traced for both modifications, also the freezing-point curve of dilute solutions.

4. The conditions under which spontaneous crystallisation of solutions of this salt takes place have been investigated, and supersolubility curves have been plotted for ice and $Na_2SO_3,7H_2O$; the extent of the metastable region in the latter case corresponds with about 30°.

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CXXXIII.—*The Rate of Formation of Azo-derivatives from Benzenoid Diamines.*

By VICTOR HERBERT VELEY.

THE rate of formation of amino- and hydroxy-azo-derivatives from diazonium salts and tertiary amines or phenols has formed the subject of a series of investigations by Goldschmidt, associated with others (*Ber.*, 1897, **30**, 670, 2075; 1900, **33**, 893; 1902, **35**, 3534). The method adopted by these authors consisted in keeping the reacting substances at a constant temperature, withdrawing aliquot portions at given intervals of time, and determining the amount of unaltered diazonium salt by measurement of the nitrogen evolved, when the solution was acidified and subsequently heated.

The general conclusions arrived at as to the first set of reactions (aminoazo-derivatives) were as follows: (i) The active material is the free base liberated by hydrolysis of its hydrochloride; (ii) the rate of formation is not influenced by the concentration of the reacting substances, but is diminished by excess of hydrochloric acid purposely added; and as to the second set of reactions (hydroxyazo-derivatives), (i) the active material is the free phenol liberated by hydrolysis; (ii) the rate of formation is diminished both by excess of alkali and increase of concentration.

Both sets of reactions are stated to be complicated instances of the second order, and the mathematical expressions proposed for their interpretation contain both a linear and a logarithmic function of a time constant.

In the above-mentioned investigations, the rate of formation of the azo-derivative was determined by a method of difference; it appeared possible that, in some cases at least, this rate might be measured directly.

Some years ago, when the author was working on the conditions of the reaction between nitric acid and certain metals (*Phil. Trans.*, 1891, *A*, **70**, 289), the well known *m*-phenylenediamine reaction for nitrous acid, originally proposed by Griess, and modified by Preusse and Tiemann, was used for the quantitative determination of small quantities of this acid.

It was found that a solution of Bismarck-brown, the dyestuff formed in the reaction, could be used as a standard, or, in other words, a variable column of such a solution was a "true * match," within limits, of the coloured solutions formed from nitrous acid and *m*-phenylenediamine hydrochloride. It was also observed that the reaction between the two last substances in sufficiently dilute solutions was gradual, requiring about half an hour for its complete development; but after an hour or more the tint gradually deepened, probably owing to some secondary change. These observations were made about eighteen years ago, and although tintometer methods have been greatly improved in the interval of time, whilst the experience of the author has been greatly increased, yet the statements originally made are found at the present date to require practically no amendment.

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* In the above text, the word "true" is used advisedly and with a set purpose, and it is desired to take the opportunity of replying to queries which have been addressed as to the real meaning of a true match of coloured solutions. It may be

In the present paper it is proposed to give an account of experiments on the rate of formation of certain azo-colouring matters by direct measurement of the amount of dyestuff found per unit time in mixed solutions of benzenoid diamines and a metallic nitrite.

EXPERIMENTAL.

The tintometer used was of the form improved with the object of cutting off extraneous light and with a suitable arrangement for the introduction of a thermometer in the box of the instrument. The fixed column adopted was 157 mm. long, which corresponded with a volume of 20 c.c. The instrument was calibrated by various coloured solutions, but it is here only necessary to cite that of Bismarck-brown. A convenient solution (about *N*/21,000) was made up, placed both into the fixed and moveable column tubes, and a match obtained; a portion of it was diluted to 0·5 and 0·25

taken that, in colorimetric methods adopted for quantitative measurements, there are two kinds of matches in tint; the one, which may be called "true" or physical, the other, "untrue" or physiological, if such expressions may be legitimately coined, without, of course, desiring to compare these two branches of natural knowledge to the possible detriment of the latter. By the former are meant solutions which would give identical absorption spectra, by the latter, solutions which would not give identical absorption spectra, but nevertheless produce sufficiently identical impressions on the retina. To take examples, a solution of Bismarck-brown is a true match of the coloured liquid formed by mixing solutions of a nitrite and *m*-phenylenediamine hydrochloride, as both contain the same dyestuff and would give identical absorption spectra, but solutions of potassium chromate and dichromate, or a solution of caramel, both of which can be made up to tints identical with solutions of Bismarck-brown, are untrue or physiological matches. It is an easy, but a frequently neglected, matter to distinguish between these two kinds of matches; if both solutions are diluted equally, in the one case, the equality of tint remains constant, and in the other, it disappears, or if one solution only be diluted, then in the one case it is matched by a column half the length of the undiluted solution, and in the other case, it is not so matched. It is to be feared that measurements supposed to be quantitative have been based upon such untrue matches without the necessary application of correction curves.

concentrations, and their tints also matched as against the moveable column of undiluted solution, six to eight observations being made in each case, the error in reading being ± 1 mm. The results are given below in abstract.

Concentration.	Fixed column, in mm.	Moveable column. Calculated, in mm.	Moveable column. Measured, in mm.	Difference, in mm.
1·0	157	157·0	157·0	nil
0·5	157	78·5	80·0	1·5
0·25	157	39·3	41·5	2·2

The greatest difference, approximately 5 per cent., occurs in the most dilute solution; this may be due either to the imperfection of the human eye, as an optical instrument, a subjective cause, or to the greater hydrolysis or ionisation of the Bismarck-brown solution, an objective cause. The author prefers the former interpretation, although others might adopt the latter.

The method of experiment was as follows: weighed quantities of the diamine hydrochloride and sodium nitrite were dissolved in water so as to form *N*/20-solutions; these were subsequently diluted to give from *N*/400, the maximum concentration, to *N*/800, the minimum concentration convenient for measurement. The dyestuff solution was made up originally of *N*/2000 strength, and subsequently diluted to about *N*/20,000. Ten c.c. of each of the reacting solutions, namely, the hydrochloride of the amine and sodium nitrite, were introduced into the "fixed column" tube, and the whole well mixed, the solution of the dyestuff was poured into the variable column tube. Observations were commenced as soon as the tint in the former was sufficiently deep for measurement, the height of the latter being about 28 mm., and this was taken as the starting point or origin of coordinates. Measurements were made at intervals of two minutes until the rate began to diminish, which generally happened about twenty minutes after the first observation, or twenty-one to twenty-three minutes after the actual time of mixture.

The unit of chemical change is taken as that amount of dyestuff formed, which corresponds with an increase of the moveable column (for the purpose of matching), expressed in terms of millimetres per minute. Thus, if Δx be the difference in height of the moveable column, and Δt the difference in time, then $\Delta x/\Delta t = k$ is the factor of the rate of chemical change. A reference to the figures given in table I will serve to make the above text clear.

The dyestuffs were obtained from Herr Grübler, of Leipzig, and the reacting substances of a high degree of purity from trustworthy firms.

Bismarck-brown from m-*Phenylenediamine Hydrochloride and Sodium Nitrite.*

The investigations of Griess (*Ber.*, 1886, **19**, 317) and Schultz (*Chemie des Steinkohlenteers.*, 2 Aufl., **2**, 193) have shown that the principal ingredient or dyestuff in commercial Bismarck-brown is bisbenzeneazophenylenediamine hydrochloride,

$$C_6H_4[N_2\cdot C_6H_3(NH_2)_2]_2,4HCl.$$

A solution of the dyestuff was made up of dilution $V=21,000$ on the assumption that the purchased sample contained 80 per cent. of the above compound. It is not, of course, material that the concentration of the solution used as the standard should be accurately known if the rate of formation is taken in units of length and not in units of dyestuff. The ratios of the factors would in both cases be the same, although the absolute numbers different.

The original solutions of the *m*-phenylenediamine hydrochloride and sodium nitrite were made up of equivalent strength, namely,

$$\tfrac{1}{2}[C_6H_4(NH_2,HCl)_2] \text{ to } NaNO_2;$$

the reaction between them commenced almost immediately after mixture.

One series of experiments is given in full in table I as illustrating the method of working; under I, the heights of the variable column of the Bismarck-brown solution expressed in millimetres, as determined at intervals of two minutes; under II, the differences, Δx, as illustrating errors of observation; under III, these differences divided by time, namely, $\Delta x/\Delta t$, or k, the factor of chemical change.

TABLE I.

Conditions of Experiment.

$$\left.\begin{array}{l}\text{10 c.c. Sodium nitrite solution, } V=600\\ \text{10 c.c. } m\text{-Phenylenediamine hydrochloride solution, } V=600\end{array}\right\}\text{mixed.}$$

Bismarck-brown solution (standard), $V=21,000$.

Temperature 11°.

I.	II.	III.	I.	II.	III.
20	—	—	124	14	7·0
32	12	6·0	136	12	6·0
45	13	6·5	148	12	6·0
58	13	6·5	161	13	6·5
71	13	6·5	175	14	7·0
84	13	6·5	189	14	7·0
97	13	6·5	201	12	6·0
110	13	6·5	213	12	6·0

It will be evident from the above figures that: (i) the error of each observation is ± 1 mm.; (ii) in this particular case the reaction continued regularly for thirty minutes without slowing down, although under other conditions the diminution of velocity was observed at an earlier stage; (iii) the rate of chemical change is a linear function of time, since $\Delta x/\Delta t = \text{constant} = 6{\cdot}4$. Of these points, only (iii) appears to require special comment. It appears probable that the chemical changes in question afford another example of a simultaneous linear reaction—to adopt a happy phrase of Jones and Richardson (Trans., 1902, **81**, 1146)—which involves the simultaneous production from one substance of at least two others, whilst the rate of formation of each of the latter is directly proportional to the amounts of the original substances present.

The course of the reactions may be explained as follows: (i) the *m*-phenylenediamine hydrochloride at the dilution used is hydrolysed almost completely into the monohydrochloride and free hydrochloric acid (Trans., 1908, **93**, 2134), and this last supplies the acid required to react with the sodium nitrite to form nitrous acid; (ii) the acid reacts with the monohydrochloride to give the bisdiazo-compound, the one product; (iii) this last reacts simultaneously, or nearly so, with a further portion of the monohydrochloride to give the bisazo-compound, the other product. These several reactions are expressible by the following equations:

(i) $C_6H_4(NH_3Cl)_2 + H_2O = NH_3Cl{\cdot}C_6H_4{\cdot}NH_3OH + HCl$ (initial hydrolysis).

(ii) $NH_3Cl{\cdot}C_6H_4{\cdot}NH_3OH + HCl + 2HNO_2 = C_6H_4(N_2Cl)_2 + 5H_2O$ (phase i).

(iii) $C_6H_4(N_2Cl)_2 + 2NH_3Cl{\cdot}C_6H_4{\cdot}NH_3OH = C_6H_4[N_2C_6H_3(NH_2)_2]_2,4HCl$ (phase ii).

It appears from experiments to be described at a future date that phase (i) is the governing factor, whether as regards its rate of formation or its subsequent decomposition when formed.

But there is, of course, the obvious difficulty that there are two and not one substance initially present, namely, the monohydrochloride and the nitrous acid (the hydrochloric acid appearing on both sides of the equations and being unaltered in mass). It may be possible that a bimolecular reaction behaves as if it were unimolecular, a by no means unusual occurrence when reactions take place at very great dilutions, so that the net result is the same, as if one substance only were present.

The secondary change alluded to in the previous and subsequent text as producing a gradual darkening in tint may be due to the formation of mononitroso-*m*-phenylenediamine hydrochloride,

$$NO{\cdot}C_6H_3(NH_3Cl)_2,$$

the conditions as to which have been studied, although not with great completeness, by Tauber and Walther (*Ber.*, 1900, **33**, 2116).

It is a further point of interest that Cain and Nicoll (Trans., 1903, **83**, 208) observed that the decomposition of certain naphthalenediazonium salts conforms, during a certain initial period, to the linear expression $\Delta x/\Delta t = k$, thus differing from the benzenediazonium salts, the decomposition of which conforms to the logarithmic expression $\log A/A - x = Kt$. The diminution of velocity subsequent to the expiry of the initial period results from a secondary change, namely, the formation of naphthaleneazonaphthols, as evidenced also by the change of colour of solution. These authors noticed that the point of change of rate depended on the mass of free hydrochloric acid, an excess of which hindered the formation of the azo-dyestuff. Although this matter may possibly be foreign to the present inquiry, yet it might be worth while to note that the author has had occasion to confirm this observation in the case of certain benzenoid azo-dyestuffs. It is hoped that the conditions of the rate of formation of other azo-dyestuffs, both from benzene and naphthalene, may be the subject of a further investigation.

But however all this may be, it is at least curious that an apparent chaos of chemical change should converge towards simplicity.

Effect of Concentration.

The effect produced by altering the concentration was studied in a series of experiments at the same temperature, namely, 11°. For the purpose of avoiding figures, so frequently identical, the results in abstract only are collected in the following table; under I are given the concentrations of reacting substances, both being equal, expressed in litres/gram-equivalents; under II, the number of observations while the reaction proceeded in its normal course, and under III, the mean value of k deduced from these observations.

TABLE II.

I.	II.	III.
400	5	17·0
500	7	12·4
600	15	6·4
700	9	4·6
800	10	2·2

From the above results it is evident that the rate decreases rapidly with dilution or increases with concentration; the former is a logarithmic function of the latter. Thus if K_1 is the factor for unit concentration, namely, $V = 800$, the factor K_n at a greater concentration, C_n, can be calculated from the expression $K_n = K_1 C_n^{2 \cdot 8}$, or $\log K_n = \log K_1 + 2 \cdot 8 \log C_n$.

The results are collated in the following table; under I are given the values of C, namely, the reciprocals of V taken in terms of the lowest; under II, the values of K_n found, and under III, those calculated by means of the above expression.

FIG. 1.

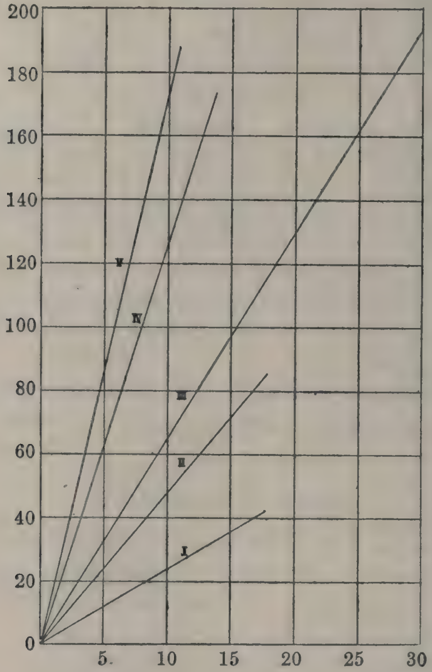


TABLE III.

I.	II.	III.
1·0	2·2	2·3
1·25	4·6	4·3
1·5	6·4	7·2
1·75	12·4	11·3
2·0	17·0	16·0

The degree of concordance of the values is as near as can be expected, having regard to the fact that for each observation there is a possible error of ± 1 mm. in the readings. The graphs are given in Fig. 1, the heights taken as ordinates and times as abscissæ.

Effect of Temperature.

As the temperature of the apparatus could not be conveniently regulated by any form of thermostat, advantage was taken of warmer weather and increased artificial warming of the working room. In these sets of experiments determinations were also made of the total amount of dyestuff, called "range" for abbreviation, which could be formed under the conditions, one hour being taken as the time-limit.

The results in abstract are set out in the table below; under I are given the values of concentration; under II, the temperatures; under III, the number of observations; under IV, the mean values of K, and under V, the ranges expressed in millimetres.

TABLE IV.

I.	II.	III.	IV.	V.
500	—	—	—	590
600	17	6	16·6	490
700	16	11	10·3	441
800	17	8	6·2	366

It was not found possible to work with the most concentrated solution, $V=400$, as the rate was too rapid for accurate working, and the tint obtained at the end of the hour modified, as previously observed, by the secondary change. On comparison of the values of K given in table IV with those in table II, it appears that the rate is a logarithmic function of absolute temperature in accordance with Esson's formula: $K_1/K=(T_1/T)^m$, or $\log K_1-\log K=m(\log T_1-\log T)$. If the value of m is taken as 45·5, the found and calculated results compare as under.

TABLE V.

$V=800.$			$V=700.$			$V=600.$		
Temp.	K (found).	K (calc.).	Temp.	K (found).	K (calc.).	Temp.	K (found).	K (calc.).
11	2·2	2·4	11	4·6	4·6	11	6·2	6·2
17	6·2	6·2	16	10·3	10·3	17	16·6	16·6

From the observations, the reaction was found to proceed normally for about twenty minutes, when about 40 per cent. of the total amount of dyestuff had been formed; it then decreased slowly. Thus, in the case of concentration $V=700$, the amount of dyestuff formed after twenty-two minutes was 235 units in millimetres; after thirty minutes was 310 units, with a mean value of $K=8·0$ (instead of 10·3) during period of eight minutes, and after sixty minutes, was 441 with a mean value of K of 4·4 during period of thirty minutes, The results are given in the graph, Fig. 2, as a single instance; those obtained in the other sets are of precisely similar type.

The range appears to be a linear function, an increase of 0·25 corresponding with an increase of 70 units, as shown in the following table.

FIG. 2.

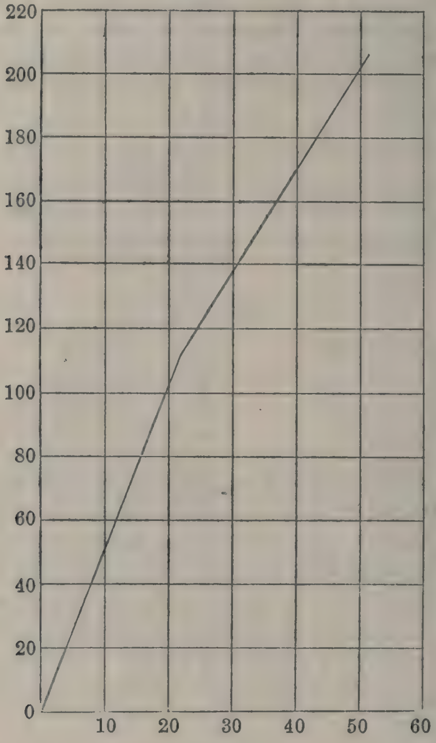


TABLE VI.

C.	Range (found).	Range (calc.).
1·0	366	366
1·25	440	436
1·5	490	506
1·75	590	576

The greatest difference between the observed and calculated values is less than 5 per cent., which is well within the probable limit of appreciation of differences in tint of highly coloured solutions.

Effect of Addition of Hydrochloric Acid.

In certain cases the effect was studied which was produced by purposely adding to the mixed solutions of sodium nitrite and *m*-phenylenediamine hydrochloride small quantities, namely, 0·1 to 0·2 c.c., of a $N/10$ solution of hydrogen chloride. The results, namely, values of K obtained, of two sets of experiments are given below; in both the concentration was the same, namely, $V = 800$, and the temperature 11°, but in (i) 0·1 c.c. and in (ii) 0·2 c.c. of $N/10$-hydrochloric acid were added.

TABLE VII.

(I.)		(II.)	
4·5	5·0	5·5	4·5
5·0	4·5	5·0	3·0
5·0	4·5	5·0	1·0
5·0	3·5	4·0	—
4·5	2·0		
5·0	1·0		

The results, taken as typical, show that the addition of hydrochloric acid produced an initial acceleration, the value of K being approximately doubled by the addition of acid (compare result in table II), but the range or limiting value is decreased in that the reaction sooner comes to an approximate end.

As regards the latter point, the above results are in accordance with the observations of Goldschmidt (*loc. cit.*) and general experience; they are the exact converse, as would appear a priori probable, of the results obtained by Cain on the effect of excess of acid on the rate of decomposition of diazonium salts (*Ber.*, 1905, **38**, 2513), which showed an initial lag (compare *Trans. Faraday Soc.*, 1909, **5**, 8).

Effect of Sulphuric Acid.

The effect produced by this acid was so very similar to that of hydrochloric acid that it appears unnecessary to give the details of the experiments in full; possibly the sulphuric acid merely serves to displace some hydrochloric acid from the hydrochloride, so the final net result would be the same for both acids.

Effect of Acetic Acid.

The results, namely, values of K, obtained in two sets of experiments are given below; in both the value of $V = 800$ was the same, and the temperature identical, 16°, but in (i) 0·05 c.c. and in (ii) 0·1 c.c. of $N/10$ acetic acid were added.

TABLE VIII.

(I.)		(II.)	
8·0	7·5	8·5	8·0
7·5	7·0	8·0	8·5
7·0	7·5	7·5	4·0
7·5	7·0	8·0	3·5
8·0	6·0	8·0	3·0
7·5	5·0	7·5	—

On comparison of these results with those obtained with same concentration, but without addition of acetic acid, it appears that this acid produces only a slight acceleration as compared with mineral acids, the values found being: (i) without acid, temp. = 17°, $K = 6·2$; (ii) with acid, temp. = 16°, $K = 8·5$; the general trend of the reaction is similar to that observed in the case of hydrochloric acid.

These results are not in accordance with the observations of Goldschmidt, who found that weak acids, such as acetic, produced a very marked acceleration.

Effect of Varying Concentration of one Reagent Only.

Two sets of experiments were conducted to study this effect, the concentration of one reacting substance being taken as double that of the other. The results are given below.

TABLE IX.

(I.)	(II.)
Concentrations.	Concentrations.
Sodium nitrite, $V=400$.	$V=800$.
Hydrochloride, $V=800$.	$V=400$.
Temp. 11°.	Temp. 11°.
K.	K.
9·0	13·0
9·5	12·0
9·5	12·0
10·0	12·5
9·0	12·0
9·0	8·5
5·0	6·5
4·5	6·5
4·5	6·0
3·0	—

In both cases the rate is initially accelerated, but remains constant for a shorter period of time. The effect is the more marked when the hydrochloride is in excess, in which case it is analogous to that produced by free hydrochloric acid; this is to be expected, as with the greater mass of hydrochloride a greater mass of hydrochloric acid is liberated by the process of hydrolysis.

Vesuvine from m-(2 : 4)*Tolylenediamine Hydrochloride and Sodium Nitrite.*

The formation of the above dyestuff, vesuvine or Manchester-brown, is quite analogous to that of Bismarck-brown, the main product being bistolueneazotolylenediamine hydrochloride,

$$C_6H_3Me[N_2\cdot C_6H_2Me(NH_2)_2]_2,4HCl.$$

A solution of the dyestuff was made up of approximate strength $V = 20,000$; the conditions and methods of working were identical with those described in the preceding section.

In the following table the results obtained are given in abstract; under I, the concentrations, both being equal, of the reagents; under II, the number of observations made while the change proceeded uniformly; under III, the values of K obtained, and under IV, the total range when its measurement was possible. The temperature was 15°, except in first series, when it was 16°.

Table X.

I.	II.	III.	IV.
400	4	16·7	—
500	7	11·6	215
600	4	6·7	188
700	9	5·0	165
800	13	2·9	130

The values of K as calculated from the logarithmic expression $K_n = K_1 C_n^{2\cdot 8}$, and the ranges as from the linear expression $\Delta = 29$ units for each increase of 0·25 concentration, are compared together in the following table.

Table XI.

C.	K_n (found).	K_n (calc.).	Range (found).	Range (calc.).
1·0	2·5	2·2	130	130
1·25	5·0	4·2	165	159
1·5	6·7	7·1	188	188
1·75	11·6	11·1	215	217
2·0	16·7	15·4	—	—

The rather high value of K obtained in the last case can probably be accounted for by slightly high temperature, namely, 1°; otherwise the concordance is within the errors of observation. On comparison with the results given in the preceding section, it is evident that (i) the rate is slightly less for the toluene than for the benzene derivative, the difference of temperature, namely, 4°, being taken into account, and (ii) the range or total amount of dyestuff capable of being formed is considerably less. It was further observed that bubbles of nitrogen gas more readily appeared, pointing to an initial decomposition of the intermediate diazonium salt.

The interpretation would appear to be that, in the case of the toluene derivative, the rate of formation of the diazo-compound is relatively greater than the consequent formation of the azo-compound; the proportion, as also the amount of the latter, would therefore be diminished. As regards the greater tendency of the former to decompose, it appears from the observations of Cain and Nicoll (Trans., 1902, 81, 1412 *et seq.*) that the rate of decomposition of *o*-toluenediazonium chloride is greater, but that of the *p*-salt less, than that of benzenediazonium chloride. Whether the steric furtherance of the amino-group in the ortho-position with respect to the methyl group is greater than the steric hindrance of the amino-group in the para-position, is a matter of probability, although, not perhaps, of certainty.

Effect of Addition of Hydrochloric Acid.

The results obtained in four sets of experiments are given below.

TABLE XII.

Volume	800	600	600	500
Hydrochloric acid added	0·2 c.c.	0·2 c.c.	1·0 c.c.	0·2 c.c.
	4·5	17	14	20
	3·5	10	nil	9 in 28 minutes
	3·0	nil	—	—
	nil	—	—	—

The above results show that, as regards the formation of vesuvine, the addition of hydrochloric acid produces a very marked initial accelerating effect, but a permanent retardation, the reaction soon coming to a conclusion; this likewise points to a decomposition of the intermediate diazonium derivative, preferentially to its further reaction to form the azo-derivative.

Effect of Varying Concentration of One Reagent Only.

The results are given below for two sets of experiments.

TABLE XIII.

Temperature 16°.

Concentrations.		
Sodium nitrite	$V=400$.	$V=800$.
Hydrochloride	$V=800$.	$V=400$.
	7·5	14·0
	8·0	15·0
	8·0	14·5
	7·5	11·5
	7·0	5·0
	7·0	3·5
	4·0	3·0

These results are perfectly analogous to those obtained in the case of Bismarck-brown (compare table IX).

Summary.

(i) The rate of formation, as studied by a tintometric method, of azo-compounds from benzenoid diamine hydrochlorides and sodium nitrite is conditioned by the hydrochloric acid and monohydrochloride liberated by hydrolysis. It is probably an example of a simultaneous, linear reaction, expressed simply as $\Delta x/\Delta t = k$.

(ii) The total amount of dyestuff capable of being formed, or range, is a linear function, but the rate a logarithmic function of the concentration expressed as $\log K_n = \log K_1 + a \log C_n$, in which a is a constant to be evaluated from the results.

(iii) The rate is a logarithmic function of absolute temperature according with the expression $K_1/k = (T_1/t)^m$.

(iv) The addition of hydrochloric acid produces an *initial* acceleration, but a *total* retardation, the reaction sooner coming to an end, and consequently the amount of dyestuff capable of being formed is thereby diminished. Other acids, such as sulphuric and acetic, produce a like effect, but in a different degree.

(v) The effect of varying the concentration of one reagent is to increase the rate; this is more marked when the hydrochloride is in excess, and is, doubtless, the result of the greater mass of hydrochloric acid liberated by hydrolysis.

(vi) The substitution of hydrogen by the methyl group (comparison of phenylene- and tolylene-diamines) causes a slight decrease in rate, but a considerable decrease in the total amount of dyestuff capable of being formed.

It is considered probable that this is a result of the more ready decomposition of the intermediate diazonium compound in the case of the latter than in that of the former. It is proposed to continue this line of investigation.

CXXXIV.—*The Molecular Weight of Tetraethylammonium Bromide and the Atomic Weight of Carbon.*

By Alexander Scott.

Twelve years ago (Trans., 1897, **71**, 550) I called the attention of the Society to the discrepancies existing amongst the various determinations of the atomic weight of carbon. The determinations which depend on the combustion of diamond, of graphite, and of pure charcoal by Dumas and Stas, by Erdmann and Marchand, by Roscoe, by C. Friedel, and by van der Plaats agree extremely well with one another and with the atomic weight deduced by physico-chemical methods from the vapour densities of several carbon compounds. These all point to the value C = 12·00 if O = 16·00. On the other hand, we have the elaborate and classical research of Stas on the conversion of carbon monoxide into the dioxide, in which both the oxygen required and the carbon dioxide produced were weighed. From this research, in which quantities of carbon dioxide weighing from 23 to 67 grams were produced in each experiment and after correction to vacuum standard, I showed (*loc. cit.*, p. 559) that C = 12·035 if we assumed the copper oxide to be quite pure and free from all nitrogen and nitrogen oxides. As it was prepared from the nitrate this was most unlikely, and allowing for the minimum amount of nitrogen at all probable, the value becomes C = 12·050. The values deduced by Liebig and Redtenbacher and others, depending on the content of silver in various silver salts of organic acids, tend to high values; taking the malate as an example, C = 12·065. This is, however, probably due to the volatility of silver at high temperatures.

Amongst the various methods which I suggested in 1897 (*loc. cit.*, p. 564) as being able to afford fresh and distinctive evidence of a valuable and extremely accurate nature was that of the titration of the hydrobromides of various organic bases against pure silver. This method had already been attempted (Dewar and Scott, *Proc. Roy. Soc.*, 1883, **35**, 347) with triethylamine. The difficulty of obtaining pure triethylamine, absolutely free from bases with lower and with higher molecular weights, together with a slight tendency of the hydrobromide to hydrolyse, prevented the attainment of results having the degree of concordance and accuracy we had hoped for. The employment of the tetra-alkylammonium bromides, as we then recognised, is much to be preferred, both because they are, relatively speaking, extremely stable, and are remarkably easy to purify in quantity.

The preliminary results which I now have the honour to bring before the Society are those made with tetraethylammonium bromide. This salt is peculiarly well adapted for a research of this nature, as its molecule contains no less than eight carbon atoms for each atom of bromine, and therefore for each atom of silver; we ought thus to be able to determine the atomic weight of carbon with an accuracy almost unparalleled even in such investigations. The salt is but slightly hygroscopic, and is stable up to about 150°, so that it can be thoroughly dried. If the temperature be raised so as to decompose the salt, as was done in experiment V, no real harm is done, as the products, ethyl bromide and triethylamine, are both easily volatile at a much lower temperature. If the bromide be converted into the hydroxide, pure triethylamine can readily be obtained, and by direct combination of this with pure ethyl bromide a new specimen of the tetraethylammonium bromide is prepared entirely from very volatile constituents, and thus a severe and crucial test can be applied to the purity of the salt. By adding bromine to the aqueous solutions of the bromide, the very insoluble perbromide is precipitated. This is also very easily purified, and from it the bromide is readily regenerated by boiling with dilute formic acid, thus:

$$(C_2H_5)_4NBr,Br_2 + H{\cdot}CO_2H = (C_2H_5)_4NBr + CO_2 + 2HBr.$$

The tetraethylammonium bromide employed in these experiments was prepared by mixing ethyl bromide and strong aqueous ammonia with almost enough absolute alcohol to retain the ethyl bromide in solution. Small quantities of a strong aqueous solution of sodium hydroxide, prepared from metallic sodium, were added at intervals of about a week, until a small excess of it remained. The reaction and the proportions employed may be represented thus:

$$4C_2H_5Br + NH_3 + 3NaHO = (C_2H_5)_4NBr + 3NaBr + 3H_2O.$$

Even by adding the soda in small portions as above, some of the ethyl bromide is, by means of the alcoholic soda, converted into ether. The yield, however, is fairly good, as from about 1830 grams of ethyl bromide, 780 grams of pure bromide were obtained, instead of 880 as indicated by theory. This was after keeping for about six weeks at the ordinary temperature.

The salt is very readily freed from the sodium bromide simultaneously produced, as it readily dissolves in, and crystallises from, absolute alcohol, in which solvent sodium bromide is practically insoluble. The addition of anhydrous ether to the solution in absolute alcohol precipitates the bromide as a very fine white powder, easily separated and dried. Any sodium bromide with which it may be contaminated in solution seems to remain almost entirely with the alcohol. The only impurity detected in the preparation employed in the following experiments was ammonium bromide, and this (as well as sodium bromide) ought to tend to lower very considerably the equivalent of the salt, and to give too low a value for the atomic weight of carbon deduced therefrom. The ammonium bromide was, however, only detected in the final mother liquors and the last crop of crystals.

The method employed to determine the molecular weight of the bromide was in every way identical with that I adopted in determining the molecular weight of ammonium bromide, and the same sample of pure silver, prepared by means of ammonium formate, was used throughout (Trans., 1901, **79**, 147). A known weight of the silver, after ignition to redness in a pure silica crucible and cooling in a current of pure hydrogen, was transferred to a stoppered bottle, and dissolved in pure nitric acid by keeping it on the water-bath for one and a-half hours. After cooling, the internal pressure is less than the atmospheric pressure, so that the stopper is readily washed into the bottle, which, after dilution of its contents, was again left on the water-bath for two to three hours until all nitrous acid and nitrogen oxides were expelled. After cooling once more, the carefully weighed quantity of the salt in almost exactly equivalent proportion was added in aqueous solution. After thorough clarification by vigorous shaking, the excess of silver or of the bromide remaining in solution was determined by means of standard solutions, which contained exactly 1 gram of metallic silver or its equivalent amount of potassium bromide per kilogram of solution. Each gram of solution was, therefore, equal to 1 milligram of silver, and one drop to 1/20th of a milligram. By this means it it easy to determine with a little practice the end point with an error not exceeding 1/10th of a milligram, or two drops of the solution.

The determinations are given in the order in which they were made, with notes as to the purification and treatment of the various samples.

A quantity of salt which had been three times crystallised from alcohol was dissolved in absolute alcohol, and the crystals which separated were reserved (expts. V and VI). The salt remaining in solution was precipitated in two fractions by the addition of anhydrous ether. It was thought that the first portion might contain any of the more insoluble impurities which might possibly be still present. The second, and much larger portion, was, therefore, taken first and titrated with the following results: 5·07039 grams of salt, dried in a vacuum, were exactly equivalent to 2·60146 grams of silver, whence it follows that $N(C_2H_5)_4Br = 210{\cdot}360$ (I).

Another portion of the same fraction, dried at 100° in a gentle current of air for six hours, gave 5·26380 grams of salt $= 2{\cdot}70142$ grams of silver, hence $N(C_2H_5)_4Br = 210{\cdot}305$ (II).

The remainder of this fraction was now dissolved in alcohol and precipitated by ether; this treatment was once more repeated, and after drying at 100°, it was found that 7·10662 grams of salt = 3·64683 grams of silver, whence $N(C_2H_5)_4Br = 210{\cdot}325$ (III).

The small fraction first precipitated from the solution was now titrated, when it was found that after drying at 100°, 6·79951 grams of salt = 3·48976 grams of silver, and $N(C_2H_5)_4Br = 210{\cdot}293$ (IV).

It was thought possible that these high numbers might have been caused in some way by the ether employed. The pure crystals above referred to as reserved were now dissolved in alcohol, and the crystals which separated were finely powdered and dried, first at 100° and then unfortunately (or perhaps fortunately), by the water-bath becoming dry, the crystals were heated until about 10 milligrams of the salt had been decomposed (160—170°). This portion had had no treatment with ether whatever, and weighed 2·72225 grams, requiring 1·39695 grams of silver, whence $N(C_2H_5)_4Br = 210{\cdot}330$ (V).

To the mother liquor from these crystals dry ether was now added, when 6·24530 grams of the dry salt thus obtained were found to be exactly equivalent to 3·20481 grams of silver, and $N(C_2H_5)_4Br = 210{\cdot}326$ (VI).

These two experiments seem to prove absolutely that the precipitation by ether has no effect on the purity of the salt, and that the uniformly high equivalent found is not due to adherent mother liquor.

The main quantity of the salt (about 500 grams) was now dissolved in alcohol, and the crystals which separated were collected, washed twice with alcohol, and redissolved, and this process repeated four times until only 40 grams remained. These were once more dissolved in hot alcohol, when 19·2 grams separated out on cooling. Of this sample, 5·74581 grams required 2·94853 grams of silver, whence $N(C_2H_5)_4Br = 210{\cdot}323$ (VII).

The addition of dry ether to the solution precipitated 19·7 grams, of which 5·21663 grams required 2·67699 grams of silver, giving a value for $N(C_2H_5)_4Br = 210{\cdot}321$ (VIII).

The mean of the first six experiments gives the value of 210·324, almost identical with that of the very pure specimens in experiments VII and VIII, one of which had been many times crystallised from alcohol, whilst the other had been precipitated by ether, the mean of these two being 210·322.

The value for the molecular weight of ammonium bromide against the identical sample of silver was 97·995. By simple subtraction and thus completely eliminating the atomic weights of bromine and nitrogen, we arrive at the equivalent of a hydrocarbon, C_8H_{16}, which is the first, as far as I know, that has been determined with a high degree of accuracy by purely chemical methods.

We have, therefore:

Tetraethylammonium bromide, $C_8H_{20}NBr$ = 210·323
Ammonium bromide, H_4NBr = 97·995

C_8H_{16} = 112·328
(H = 1·0075) H_{16} = 16·120

C_8 = 96·208
C = 12·026

A small quantity of tetramethylammonium bromide was prepared from a very pure specimen of the iodide by treatment with silver oxide, and neutralising the solution of the hydroxide obtained with pure hydrobromic acid. This salt crystallises well from water, and is much less hygroscopic than the corresponding ethyl salt, and resists a considerably higher temperature. Of this sample crystallised from water, 8·64585 grams required 6·05348 grams of silver, whence $N(CH_3)_4Br$ = 154·150 and C_4H_8 = 56·155. This with H_8 = 8·060 gives C_4 = 48·095 and C = 12·024.

All the foregoing weighings are corrected for errors in the face values of the weights, and are reduced to vacuum standard. The equivalents given above are calculated for Ag = 107·93, as they are then more easily comparable with the work of Stas and others. This value is in all probability notably high, and taking the value 107·88 for the atomic weight of silver, we get the following values:

NH_4Br = 97·950
$N(CH_3)_4Br$ = 154·079 and C = 12·017
$N(C_2H_5)_4Br$ = 210·226 and C = 12·019

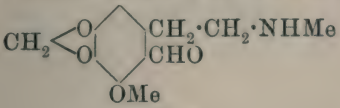
The value 107·88 can hardly be regarded as the final value for the atomic weight of silver, but any further lowering of this value cannot have much effect on the number obtained for the atomic weight of carbon determined in this way.

THE DAVY-FARADAY LABORATORY
OF THE ROYAL INSTITUTION.

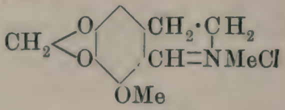
CXXXV.—*The Synthesis of Substances Allied to Cotarnine.*

By ARTHUR HENRY SALWAY.

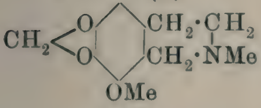
IN the course of a recent investigation on the constituents of the essential oil of nutmeg (Power and Salway, Trans., 1907, **91**, 2037), amongst other compounds, a considerable quantity of myristicin was isolated. It seemed probable that this substance would serve as a convenient starting-point for the synthesis of cotarnine, the constitution of which has been the subject of considerable discussion. Roser (*Annalen*, 1888, **249**, 156), on the one hand, in consideration of the fact that cotarnine behaves both as an aldehyde and a secondary amine, assigns to it the formula (I), whilst its hydrochloride, which is formed with elimination of the elements of water, is given the formula (II). Decker (*J. pr. Chem.*, 1893, [ii], **47**, 222), on the other hand, draws attention to the improbability of the co-existence of an aldehydic residue and a secondary amino-group in the same molecule, and points out that Roser's formula does not explain why cotarnine is precipitated from its hydrochloride in the aldehydic form, or why hydrocotarnine (III) is converted into cotarnine on oxidation. For these reasons, Decker proposes formula (IV).



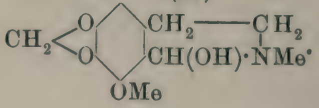
(I.)



(II.)

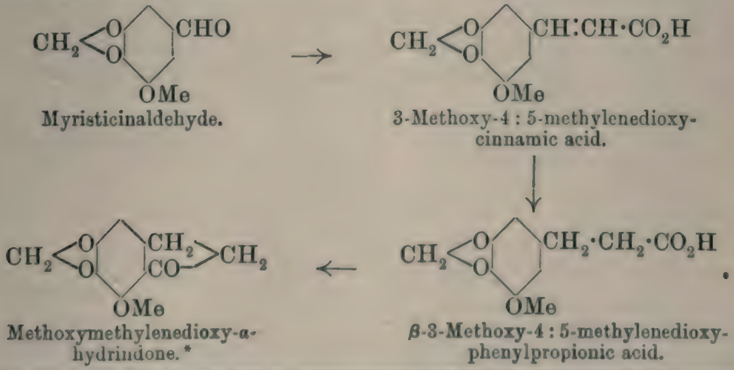


(III.)



(IV.)

With the object of effecting the synthesis of cotarnine from myristicin, the first experiments consisted in preparing methoxymethylenedioxy-α-hydrindone, which was obtained according to the following scheme of reactions:



Myristicinaldehyde.

3-Methoxy-4 : 5-methylenedioxycinnamic acid.

β-3-Methoxy-4 : 5-methylenedioxyphenylpropionic acid.

Methoxymethylenedioxy-α-hydrindone.*

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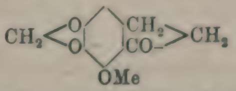
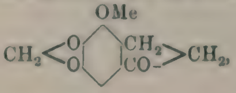
* Of the two possible formulæ for methoxymethylenedioxy-α-hydrindone, namely:



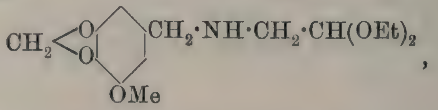
and



the former has been adopted throughout this communication. The same applies to

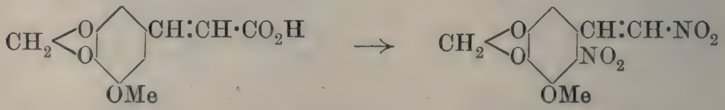
Attempts to convert the oxime of methoxymethylenedioxy-α-hydrindone into 1-hydroxy-8(5)-methoxy-6 : 7-methylenedioxydihydro*iso*quinoline by means of the Beckmann transformation were unsuccessful, so that the synthesis of cotarnine from this compound by subsequent methylation and reduction could not be effected.

A further attempt to apply the Pomeranz (*Monatsh.*, 1893, **14**, 118; 1894, **15**, 301) *iso*quinoline synthesis to myristicinaldehyde was also unsuccessful, because the condensation of myristicinylideneaminoacetal could not be effected on account of the readiness with which the substance is reconverted into its components, myristicinaldehyde and aminoacetal. In order to obviate this disruption of the molecule, myristicinylideneaminoacetal was first reduced to myristicinylaminoacetal,



and the latter then subjected to the action of sulphuric acid and other condensing agents under varied conditions. In this case, also, the reaction did not proceed in the desired direction, and only resinous products were formed.

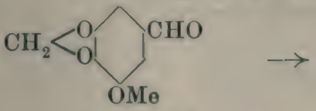
Finally, some experiments were conducted which led to the synthesis of a number of substances allied to cotarnine. It was necessary, in the first place, to prepare 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamic acid, and for this purpose myristicinaldehyde was converted by means of sodium and ethyl acetate into 3-methoxy-4 : 5-methylenedioxycinnamic acid; the action of nitric acid on this substance, however, leads to the displacement of the carboxyl group by a nitro-group, and at the same time a nitro-group is introduced into the nucleus:



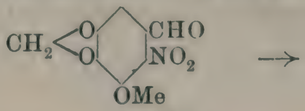
A second method for the preparation of 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamic acid was more successful. Myristicinaldehyde (V) on nitration yields a mixture of 5-nitro-1-methoxy-2 : 3-methylenedioxybenzene and nitromyristicinaldehyde (VI) (this vol., p. 1160), the latter of which readily condenses with sodium acetate and acetic anhydride with the formation of 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamic acid (VII).

the alternative formulæ in the case of nitromethoxymethylenedioxycinnamic acid, ketomethoxymethylenedioxydihydroquinoline, oxy*iso*cotarnine, etc.

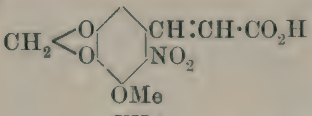
Methyl 2(6)-nitro-3-methoxy-4:5-methylenedioxycinnamate is readily reduced to the corresponding amino-compound, which, in the presence



(V.)

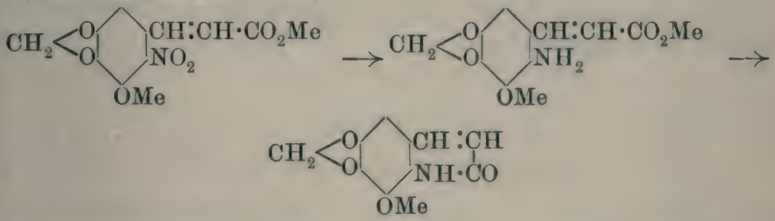


(VI.)



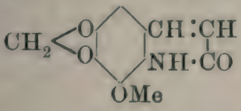
(VII.)

of acids, is transformed into 2-keto-8(5)-methoxy-6 : 7-methylenedioxy-1 : 2-dihydroquinoline (VIII).

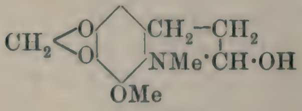


(VIII.)

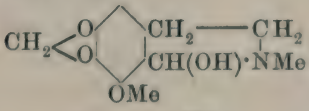
2-Keto-8(5)-methoxy-6 : 7-methylenedioxy-1 : 2-dihydroquinoline is of considerable interest on account of its relationship to cotarnine (X). If the formulæ of the two substances are compared, it would appear possible to convert the former by reduction and methylation into an isomeride of cotarnine, which might appropriately be designated *iso*cotarnine (IX).



(VIII.)

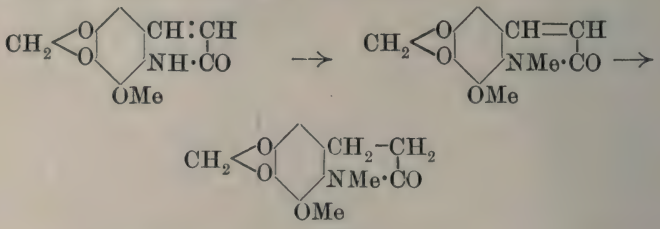


(IX.)



(X.)

2-Keto-8(5)-methoxy-6 :7-methylenedioxy-1 :2-dihydroquinoline, however, polymerises so easily on reduction, either in acid or in alkaline solution, that it was found impossible to prepare the unimolecular reduction product. In this respect its behaviour is similar to that of carbostyril itself towards reducing agents, as Friedländer and Müller (*Ber.*, 1887, **20**, 2012) have shown. In order to avoid this polymerisation, 2-keto-8(5)-methoxy-6 : 7-methylenedioxy-1 : 2-dihydroquinoline was methylated, and yielded, according to the conditions of the reaction, either an *O*- or a *N*-methyl ether. By the reduction of the latter compound, oxy*iso*cotarnine (XI) was obtained.



(XI.)

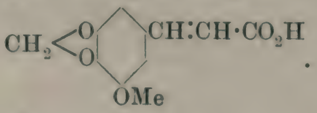
All efforts to reduce this compound to *iso*cotarnine were unsuccessful. The physiological action of the above-mentioned substances is at present under investigation.

EXPERIMENTAL.

Preparation of Myristicinaldehyde.

Myristicin (5 parts) was heated for twenty-four hours on the water-bath with a solution of potassium hydroxide (4 parts) in 15 parts of alcohol, whereby a quantitative yield of *iso*myristicin was obtained (compare Semmler, *Ber.*, 1891, **24**, 3818; Thoms, *Ber.*, 1903, **36**, 3446). The latter substance, in portions of 10 grams at a time, was then shaken into an emulsion with water at 60°, and a solution of 20 grams of potassium permanganate in 500° c.c. of water gradually added with constant agitation, the temperature being kept at 60—65°. After all the permanganate had been added, for which about an hour was necessary, the mixture was cooled, filtered, and the manganese precipitate well washed with cold water. The precipitate, which contained the myristicinaldehyde, was dried on a porous plate, and afterwards extracted in a Soxhlet apparatus with chloroform. The chloroform extracts from several such oxidations were united, the solvent removed, and the solid residue well washed with cold ether to remove unoxidised *iso*myristicin. The yield of myristicinaldehyde was 40—45 per cent. of the *iso*myristicin employed. A quantity of myristicinic acid, varying from 15 to 20 per cent., was always formed by the oxidation, and could be obtained by acidifying the filtrate from the manganese precipitate.

3-*Methoxy*-4 : 5-*methylenedioxycinnamic Acid*,



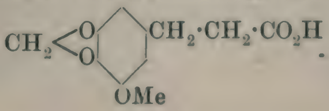
One hundred and fifty grams of myristicinaldehyde were dissolved in 400 grams of ethyl acetate, and to this solution 37·5 grams of sodium, finely divided by vigorous agitation with boiling toluene, were added. The violent reaction which immediately ensued was moderated by cooling the mixture. When the action had subsided, the mixture was kept at the ordinary temperature for some time, after which the product was hydrolysed by heating for half an hour with an excess of alcoholic potash. The alcohol was then removed as completely as possible, water added, and the alkaline liquid extracted with chloroform to remove resinous matter. On acidifying with dilute sulphuric acid, a grey precipitate was obtained, which was crystallised from glacial acetic acid. The yield of methoxymethylenedioxycinnamic acid was 137 grams:

0·1342 gave 0·2914 CO_2 and 0·0554 H_2O. $C = 59·2$; $H = 4·6$.

$C_{11}H_{10}O_5$ requires $C = 59·5$; $H = 4·5$ per cent.

3-*Methoxy*-4 : 5-*methylenedioxycinnamic acid* is readily soluble in hot acetic acid, from which, on cooling, it crystallises in well-formed, colourless, prismatic needles, sintering at 220° and melting and decomposing at 228°. It is only moderately soluble in boiling alcohol, and is deposited from this solvent in thin, flat plates. It is practically insoluble in water and only very sparingly soluble in ether.

β-3-*Methoxy*-4 : 5-*methylenedioxypropionic Acid*,

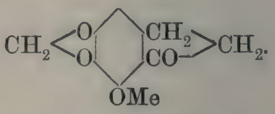


Fifty grams of 3-methoxy-4 : 5-methylenedioxycinnamic acid were dissolved in dilute sodium hydroxide, and reduced with 800 grams of sodium amalgam (4 per cent.) at the ordinary temperature. The liquid was mechanically stirred throughout the reduction, whilst the accumulation of alkali in the mixture was prevented by the periodic addition of hydrochloric acid. At the end of the reaction the alkaline liquid was acidified and the precipitated oil extracted with ether, when, on evaporating the solvent, a viscid, brown oil was obtained. This solidified after long keeping, and was then crystallised from benzene and alcohol. The yield of this substance amounted to 60 per cent. of the 3-methoxy-4:5-methylenedioxycinnamic acid employed:

0·1300 gave 0·2804 CO_2 and 0·0672 H_2O. $C=58·8$; $H=5·7$.
$C_{11}H_{12}O_5$ requires $C=58·9$; $H=5·4$ per cent.

β-3-Methoxy-4:5-methylenedioxypropionic acid is only sparingly soluble in benzene, light petroleum, or chloroform, but it is readily soluble in ether, ethyl acetate, or hot water, and extremely so in alcohol, acetone, or acetic acid. It crystallises with difficulty. If dissolved in hot benzene to which a few drops of alcohol have been added, it is deposited, after a long time, in hard, colourless, crystalline nodules melting at 124—125°.

Methoxymethylenedioxy-α-hydrindone,



Twenty grams of β-3-methoxy-4:5-methylenedioxypropionic acid were dissolved in boiling benzene (300 c.c.), and 100 grams of phosphoric oxide gradually added with constant agitation. The mixture was heated for several hours on the water-bath, after which the dark red phosphorus compound was removed by decantation and decomposed by adding ice-water. The aqueous mixture was extracted repeatedly with ether, the ethereal solution washed successively with sodium hydroxide and water, dried, and the ether removed. A pale yellow, crystalline solid remained, which separated from alcohol in slender, colourless needles, melting at 141—142°:

0·1256 gave 0·2967 CO_2 and 0·0575 H_2O. $C=64·4$; $H=5·1$.
$C_{11}H_{10}O_4$ requires $C=64·1$; $H=4·9$ per cent.

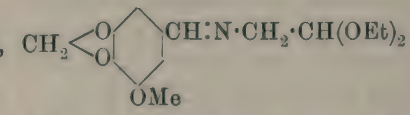
Methoxymethylenedioxy-α-hydrindone is easily soluble in ether and benzene, and crystallises from these solvents in well-formed, prismatic needles. The *oxime*, prepared in the usual way, is only very sparingly soluble in hot alcohol or ethyl acetate, and crystallises from these solvents in small, colourless needles, decomposing at about 250°. In benzene, ether, chloroform, or light petroleum it is practically insoluble:

0·1057 gave 0·2320 CO_2 and 0·0496 H_2O. $C=59·9$; $H=5·2$.
$C_{11}H_{11}O_4N$ requires $C=59·7$; $H=5·0$ per cent.

The Beckmann transformation could not be effected in the case of this oxime; phosphorus pentachloride, in the presence of dry ether, is without any action on it, whilst with the use of benzene as solvent, on heating, a vigorous reaction ensues, with the formation of a carbonaceous mass, from which nothing definite could be isolated. Other reagents, such as sulphuric acid, phosphoric oxide, and acetyl chloride, were also employed, but in no case was it possible to isolate any crystalline product.

The above experiments for the synthesis of cotarnine not having proved successful, a second method was tried, which has already been applied by Fritsch (*Annalen*, 1895, **286**, 18) to the synthesis of hydrastinine. This consisted in the condensation of myristicinylideneaminoacetal to the corresponding *iso*quinoline derivative; the latter, by reduction and methylation, should then be converted into hydrocotarnine.

Myristicinylideneaminoacetal,



Twenty grams of aminoacetal and 27 grams of myristicinaldehyde were heated together at 100° for two hours, when the reaction was complete. The product was then dissolved in ether, the ethereal solution being washed with water, dried, and the solvent removed. The viscid, brown oil thus obtained was purified by distillation under diminished pressure:

0·1260 gave 0·2819 CO_2 and 0·0840 H_2O. C = 61·0 ; H = 7·4.

$C_{15}H_{21}O_5N$ requires C = 61·0 ; H = 7·1 per cent.

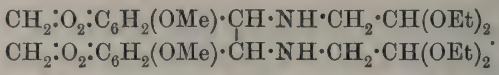
Myristicinylideneaminoacetal is a colourless, viscid oil, which does not solidify at −20°. It distils at 234°/15 mm. and 244°/25 mm. It is readily miscible with ether, alcohol, or chloroform, but only sparingly soluble in petroleum. It dissolves in dilute mineral acids, but is soon resolved into its components, myristicinaldehyde being precipitated. Owing to the readiness with which myristicinylideneaminoacetal undergoes this change, it was found impossible to prepare from it the desired methoxymethylenedioxy*iso*quinoline. Thus, when myristicinylideneaminoacetal was added, drop by drop, to ice-cold sulphuric acid (75 per cent.), it was rapidly converted into myristicinaldehyde, and no trace of methoxymethylenedioxy*iso*quinoline could be detected in the product. With the object of preventing this disruption of the molecule under the influence of acids, myristicinylideneaminoacetal was reduced to myristicinylaminoacetal, but this compound, also, could not be condensed to methoxymethylenedioxydihydro*iso*quinoline.

Reduction of Myristicinylideneaminoacetal.

Twenty grams of myristicinylideneaminoacetal were dissolved in dilute alcohol, and the solution well agitated with 4 grams of amalgamated aluminium granules. After several hours the precipitated aluminium hydroxide was removed by filtration, and the alcoholic filtrate treated as before with a fresh portion (4 grams) of aluminium amalgam. The mixture was then filtered, and the alcohol removed as completely as possible from the filtrate, when a brown oil was precipitated. This was extracted with ether, the ethereal solution being dried, and the solvent removed. The residual oil, on agitation with light petroleum, deposited a small proportion of a solid substance, which was crystallised from a mixture of benzene and light petroleum. It separated from this solvent in slender, colourless needles, melting at 128°. The yield of this substance amounted to 10 per cent. of the material employed :

0·1205 gave 0·2672 CO_2 and 0·0808 H_2O. $C = 60·5$; $H = 7·5$.
0·0767 „ 0·1710 CO_2 „ 0·0550 H_2O. $C = 60·8$; $H = 8·0$.
0·1455 „ 6·3 c.c. N_2 at 13·5° and 768 mm. $N = 5·2$.
0·2511, in 24·47 benzene, gave Δt $-0·088°$. M.W. = 583.
$C_{30}H_{44}O_{10}N_2$ requires $C = 60·8$; $H = 7·4$; $N = 4·7$ per cent. M.W. = 592.

It is evident from these results that the above compound has been formed by the association and reduction of two molecules of myristicinylideneaminoacetal. Its constitution may therefore be represented as :



$$\begin{array}{l} CH_2{:}O_2{:}C_6H_2(OMe)\cdot CH\cdot NH\cdot CH_2\cdot CH(OEt)_2 \\ \qquad\qquad\qquad\qquad\quad | \\ CH_2{:}O_2{:}C_6H_2(OMe)\cdot CH\cdot NH\cdot CH_2\cdot CH(OEt)_2 \end{array}.$$

The compound is extremely soluble in the usual organic solvents, with the exception of light petroleum. It dissolves also in cold dilute mineral acids without change, but on warming the solution the substance is rapidly decomposed, with the deposition of resinous matter and the production of a claret-red colour. In concentrated sulphuric acid it gives a beautiful violet coloration.

In the above reduction of myristicinylideneaminoacetal the chief product was an oil, from which the above compound melting at 128° had been removed by means of petroleum. This oil distilled at 240°/27 mm. as a colourless liquid :

0·1200 gave 0·2646 CO_2 and 0·0830 H_2O. $C = 60·1$; $H = 7·7$.
0·2733 „ 10·8 c.c. N_2 at 18° and 758 mm. $N = 4·6$.
$C_{15}H_{23}O_5N$ requires $C = 60·6$; $H = 7·7$; $N = 4·7$ per cent.

This substance, evidently myristicinylaminoacetal,

$$CH_2{:}O{:}C_6H_2(OMe)\cdot CH_2\cdot NH\cdot CH_2\cdot CH(OEt)_2,$$

is a colourless oil, which is readily miscible with benzene, alcohol, ether, or ethyl acetate, but is only sparingly soluble in light petroleum. It dissolves unchanged in cold dilute mineral acids, but on heating the solution it decomposes, with the production of a claret-red coloration. Its *hydrochloride* may be prepared by dissolving the base in cold dilute hydrochloric acid, and allowing the solution to evaporate spontaneously over potassium hydroxide in a vacuum. The crystalline solid, which is gradually deposited, may be recrystallised from a mixture of ethyl acetate and alcohol, when it separates in well-formed, colourless plates, melting and decomposing at 133°:

0·1672 gave 0·0704 AgCl. Cl = 10·4.

$C_{15}H_{23}O_5N,HCl$ requires Cl = 10·6 per cent.

This hydrochloride is readily soluble in water and alcohol, but insoluble in ethyl acetate.

With the object of preparing methoxymethylenedioxydihydro*iso*quinoline from myristicinylaminoacetal, 5 grams of the latter were added, drop by drop, to 20 c.c. of sulphuric acid (75 per cent.) at 0°. The first addition of the myristicinylaminoacetal produced an intense violet coloration, which on further addition was changed to deep red. The mixture was kept for two days at the ordinary temperature, and then neutralised by the cautious addition of alkali, when a brown, amorphous precipitate was formed. This was soluble in acids, but insoluble in the ordinary organic solvents, and constituted the sole product of the reaction, no methoxymethylenedioxydihydro*iso*quinoline having been produced.

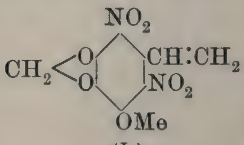
Another portion of myristicinylaminoacetal was dissolved in cold concentrated hydrochloric acid, and the solution kept at the ordinary temperature for forty-eight hours. It was then diluted with water and extracted with ether, which removed a small quantity of a brown solid. On dissolving the latter in a mixture of benzene and petroleum, a few colourless needles separated, which melted at 138°, but the amount of this substance was not sufficient for further examination. The acid liquid which had been extracted with ether was rendered alkaline, when a brown, amorphous, insoluble resin separated, from which nothing definite could be isolated. It formed, with the exception of the small amount of crystalline substance mentioned above, the sole product of the reaction. This method is therefore inapplicable for the synthesis of cotarnine and allied compounds.

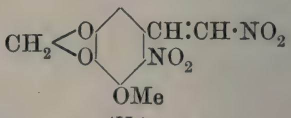
The Action of Nitric Acid on 3-*Methoxy*-4 : 5-*methylenedioxycinnamic Acid.*

Ten grams of 3-methoxy-4 : 5-methylenedioxycinnamic acid were added in small quantities at a time to 50 c.c. of nitric acid (sp. gr. 1·41) cooled in a freezing mixture. The liquid at first became yellow, but soon acquired a deep red colour, and after a short time carbon dioxide was slowly evolved. The mixture was kept in the cold for half an hour, then poured into ice-water, and the resulting yellow precipitate collected and washed. This was digested with ether, and the insoluble portion, consisting of unchanged 3-methoxy-4 : 5-methylenedioxycinnamic acid, removed by filtration. The ethereal filtrate was washed successively with aqueous sodium hydroxide and water, dried, and the solvent removed. The residual solid crystallised from alcohol in slender, lemon-yellow needles, melting at 148°:

0·1014 gave 0·1682 CO_2 and 0·0296 H_2O. C = 45·2; H = 3·2.
0·0777 ,, 7·4 c.c. N_2 at 23° and 766 mm. N = 10·9.
$C_{10}N_8O_7N_2$ requires C = 44·8; H = 3·0; N = 10·5 per cent.

Considering the method of preparation, it is evident that the substance must be represented by one of the two following formulæ:


(I.)


(II.)

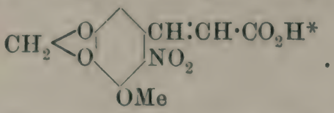
It was possible to decide between these formulæ by examining the product of oxidation. A small quantity of the compound melting at 148° was oxidised with hot alkaline permanganate, and at the end of the reaction sulphur dioxide was passed into the hot mixture until the manganese precipitate had redissolved. On cooling, slender needles were deposited, which melted and decomposed at 245°. Both by analysis and by the mixed melting-point method, it was proved that this compound was identical with nitromyristicinic acid (this vol., p. 1165):

0·0714 gave 0·1170 CO_2 and 0·0231 H_2O. C = 44·7; H = 3·6.
$C_9H_7O_7N$ requires C = 44·8; H = 2·9 per cent.

The compound melting at 148° is therefore ω-2(6)-dinitro-3-methoxy-4:5-methylenedioxystyrene; its formation from 3-methoxy-4:5-methylenedioxycinnamic acid is evidently due to the direct displacement of the carboxyl group by a nitro-group, with the simultaneous introduction of a second nitro-group into the nucleus. The same type of reaction has recently been shown by the author (this vol., p. 1155) to be common to the ethers of aromatic hydroxyaldehydes and hydroxy-acids, but the present example is of additional interest, since it shows that the reaction is not exclusively confined to those compounds in which the carboxyl group is directly attached to the benzene nucleus.

ω-2(6)-*Dinitro*-3-*methoxy*-4:5-*methylenedioxystyrene* is readily soluble in the usual organic solvents. It possesses feebly acidic properties. When warmed with aqueous sodium hydroxide it dissolves with difficulty, but on the addition of a few drops of alcohol it readily passes into solution with a deep yellow colour, and is reprecipitated by hydrochloric acid.

2(6)-*Nitro-3-methoxy-*4 : 5-*methylenedioxycinnamic Acid,*



Fifty grams of finely powdered nitromyristicinaldehyde, prepared by the nitration of myristicinaldehyde (this vol., p. 1160), were intimately mixed with 26 grams of fused sodium acetate, and 100 c.c. of acetic anhydride added. After heating in an oil-bath at 160° for six hours, the mixture was allowed to cool, then digested with an excess of ammonia until nothing further dissolved, and the red solution extracted once with ether to remove resinous by-products. On acidifying the ammoniacal solution, 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamic acid was obtained as a yellow precipitate, which was washed with water and crystallised from acetic acid. The yield amounted to 84 per cent. of the aldehyde employed :

0·1231 gave 0·2240 CO_2 and 0·0410 H_2O. $C = 49·6$; $H = 3·7$.

0·2168 required for neutralisation 8·05 c.c. N/10-NaOH. M.W. (for a monobasic acid) = 269.

$C_{11}H_9O_7N$ requires $C = 49·4$; $H = 3·4$ per cent. M.W. = 267.

2(6)-*Nitro-3-methoxy-*4 : 5-*methylenedioxycinnamic acid* crystallises from hot acetic acid in small, yellow plates, which decompose, when heated to 260°, with the formation of a carbonaceous mass. It is only moderately soluble in alcohol, from which, however, it separates in stout, deep yellow prisms.

Methyl-2(6)-*nitro-3-methoxy-*4 : 5-*methylenedioxycinnamate* was prepared by passing a current of dry hydrogen chloride for one and a-half hours into a hot mixture of methyl alcohol and the acid. It crystallises from a mixture of alcohol and ethyl acetate in long, yellow needles, melting at 192°. The *ethyl* ester, prepared in a similar manner, also crystallises in beautiful, yellow needles, melting at 166°.

Methyl 2(6)-*amino-3-methoxy-*4 : 5-*methylenedioxycinnamate,*

$$CH_2{:}O_2{:}C_6H(OMe)(NH_2)\cdot CH{:}CH\cdot CO_2Me.$$

—Three grams of methyl 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamate were finely powdered and gently warmed on the water-bath for half-an-hour with a solution of stannous chloride (12 grams) in concentrated hydrochloric acid (36 c.c.), when the powdered nitro-compound had become changed into a crystalline hydrochloride. This was collected, washed with cold concentrated hydrochloric acid, dissolved in cold water, and the free base precipitated by the addition of sodium hydroxide. It crystallised from alcohol in brilliant yellow, slender needles, melting at 153°:

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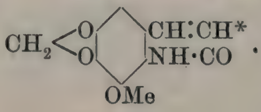
* See footnote on p. 1205.

0·0817 gave 0·1722 CO_2 and 0·0432 H_2O. C = 57·5; H = 5·9.
$C_{12}H_{13}O_5N$ requires C = 57·4; H = 5·2 per cent.

Methyl 2(6)-amino-3-methoxy-4 : 5-methylenedioxycinnamate dissolves in alcohol, chloroform, or ethyl acetate with the formation of a deep yellow colour, but the solution in acids is colourless. When warmed with dilute hydrochloric acid, hydrolysis and condensation occur, and the ester is converted into ketomethoxymethylenedioxydihydroquinoline.

2-*Keto*-8(5)-*methoxy*-6 : 7-*methylenedioxy*-1 : 2-*dihydroquinoline*,



This compound is best prepared directly from methyl 2(6)-nitro-3-methoxy-4 : 5-methylenedioxycinnamate without the isolation of the intermediate amino-compound. This ester (10 grams) was dissolved in alcohol, and reduced by heating for two hours with a solution of stannous chloride (50 grams) in 150 c.c. of concentrated hydrochloric acid. The alcohol was then removed as completely as possibly, and the mixture poured into water, when a crystalline solid separated, which was recrystallised from water and dried at 105°:

0·1055 gave 0·2340 CO_2 and 0·0420 H_2O. C = 60·5; H = 4·5.
$C_{11}H_9O_4N$ requires C = 60·3; H = 4·1 per cent.

The compound crystallises from hot water in long, silky needles, which melt at 181—182° and contain half a molecule of water of crystallisation:

1·9723 lost, at 105°, 0·0826 H_2O. H_2O = 4·2.
$C_{11}H_9O_4N,\frac{1}{2}H_2O$ requires H_2O = 3·9 per cent.

It is readily soluble in hot alcohol or chloroform, from which it separates in radiating clusters of slender needles. It exhibits both feebly acidic and basic properties. Thus it dissolves in concentrated hydrochloric acid with the formation of a *hydrochloride*, which separates in colourless leaflets decomposing at 225°; on the addition of water the base is regenerated. It is also soluble in concentrated aqueous sodium hydroxide, but is reprecipitated by water.

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* See footnote on p. 1205.

Reduction of 2-*Keto*-8(5)-*methoxy*-6 : 7-*methylenedioxy*-1 : 2-*dihydroquinoline.*

Two grams of the substance were dissolved in dilute alcohol and reduced by the action of 200 grams of sodium amalgam (3½ per cent.) with constant stirring. After a short time a grey precipitate separated, and the liquid gradually acquired a red colour. When the reaction was complete, the grey precipitate was removed by filtration and washed with water. It was insoluble in acids or alkalis, and practically so in ethyl acetate, chloroform, alcohol, or ether, but could be crystallised from hot acetic acid, from which it separated in small, colourless needles. These did not melt when heated to 310°:

0·0905 gave 0·1994 CO_2 and 0·0400 H_2O. C = 60·1; H = 4·9.

$(C_{11}H_{10}O_4N)_x$ requires C = 60·0; H = 4·5 per cent.

It is evident from the properties of this compound that its formation is due to polymerisation and simultaneous reduction of the ketomethoxymethylenedioxydihydroquinoline.

The alkaline filtrate from which the above compound had been separated was heated on the water-bath to remove alcohol, and then acidified with dilute hydrochloric acid, when a colourless substance was precipitated. This was collected, washed, and crystallised from dilute acetic acid, from which it was deposited in colourless needles, melting at 290°. It was very sparingly soluble in water or alcohol, but more soluble in chloroform:

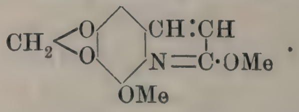
0·1051 gave 0·2307 CO_2 and 0·0439 H_2O. C = 59·9; H = 4·6.

$(C_{11}H_{10}O_4N)_x$ requires C = 60·0; H = 4·5 per cent.

The analysis and the properties of this substance show that it possesses the same empirical formula as the previously isolated compound, and is likewise a polymerised reduction product of ketomethoxymethylenedioxydihydroquinoline. No other substance could be isolated from the products of this reaction.

Ketomethoxymethylenedioxydihydroquinoline was next reduced by means of sodium amalgam in dilute acetic acid solution, but in this case, also, the chief products were the above-described polymerised compounds, melting at 290° and above 310° respectively. A small amount of substance melting at 120° was obtained, but not sufficient for its further examination.

8(5)-*Methoxy*-6 : 7-*methylenedioxycarbostyril Methyl Ether*,



In order to avoid, if possible, formation of the above polymerised products, the methyl derivatives of 2-keto-8(5)-methoxy-6 : 7-methylenedioxy-1 : 2-dihydroquinoline were prepared prior to reduction.

Equal parts of ketomethoxymethylenedioxydihydroquinoline and methyl iodide were dissolved in chloroform, and the solution heated on the water-bath for several hours in the presence of dry silver oxide (1 part). The liquid was then filtered, shaken successively with sodium hydroxide and water, dried, and the solvent removed. The solid residue was crystallised from alcohol, when it separated in stellar clusters of needles, melting at 113°:

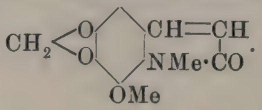
0·0706 gave 0·1600 CO_2 and 0·0326 H_2O. C = 61·8 ; H = 5·1.

$C_{12}H_{11}O_4N$ requires C = 61·8 ; H = 4·7 per cent.

That this substance is the *O*-methyl ether is proved by its behaviour on heating with methyl iodide. Thus, when heated for three hours at 120° with an excess of methyl iodide in a sealed tube, it is quantitatively converted into the isomeric *N*-methyl ether described below (compare Knorr, *Ber.*, 1897, **30**, 929).

8(5)-*Methoxy*-6 : 7-*methylenedioxycarbostyril methyl ether* crystallises from concentrated alcoholic solution in slender needles, whilst from more dilute solutions it separates in hexagonal prisms. It is only sparingly soluble in hot water, from which it is deposited in silky needles. It possesses much stronger basic properties than the parent compound, since its hydrochloride is not dissociated in dilute aqueous solution. It is not changed by heating for several hours at 100° with 20 per cent. hydrochloric acid, but when heated with concentrated hydrochloric acid in a sealed tube it is completely decomposed, with the formation of a dark violet-coloured, resinous mass.

2-*Keto*-8(5)-*methoxy*-6 : 7-*methylenedioxy*-1-*methyl*-1 : 2-*dihydroquinoline*,



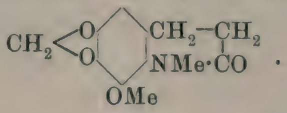
This substance, as above indicated, may be prepared from the isomeric *O*-methyl ether by heating with methyl iodide. It was also prepared directly from ketomethoxymethylenedioxydihydroquinoline by the following method. Two grams of the substance, dissolved in methyl alcohol, were heated for several hours with an excess of methyl iodide and sodium methoxide. The methyl alcohol was then removed, water added to the residue, and the mixture extracted with chloroform. The chloroform solution was washed, dried, and the solvent removed, when a solid residue was obtained which crystallised from alcohol in well-formed, colourless needles, melting at 179° :

0·0904 gave 0·2045 CO_2 and 0·0379 H_2O. C = 61·7 ; H = 4·7.

$C_{12}H_{11}O_4N$ requires C = 61·8 ; H = 4·7 per cent.

This compound possesses only feebly basic properties, and is insoluble in cold dilute hydrochloric acid.

*Oxy*isocoturnine (2-*Keto*-8(5)-*methoxy*-6 : 7-*methylenedioxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*).



One gram of the compound just described was reduced in dilute alcoholic solution by means of 200 grams of sodium amalgam (3 per cent.). During the course of the reaction the mixture was constantly agitated, and from time to time small quantities of hydrochloric acid were added to prevent the accumulation of alkali in the solution. After a short time a small quantity of solid separated, which at the end of the reaction was collected. It was only sparingly soluble in hot alcohol, from which it crystallised in rhombohedral prisms, melting at 280°. This substance was apparently a polymerised reduction product, similar in character to the products of high molecular weight obtained on reducing ketomethoxymethylenedioxydihydroquinoline.

The filtrate from which the above compound had been separated was acidified with dilute hydrochloric acid, distilled in a current of steam to remove the alcohol, then rendered alkaline, and extracted with ether. This removed a viscid oil, which rapidly solidified, and when crystallised from dilute alcohol, separated in flat plates, melting at 113° :

0 0881 gave 0·1982 CO_2 and 0·0447 H_2O. C = 61·4 ; H = 5·6.

$C_{12}H_{13}O_4N$ requires C = 61·3 ; H = 5·5 per cent.

It is evident from these results that the reduction of 2-keto-8(5)-methoxy-6 : 7-methylenedioxy-1-methyl-1 : 2-dihydroquinoline by means of sodium amalgam effects the addition of two atoms of hydrogen only. The product, therefore, is isomeric with oxycotarnine.

*Oxy*isocotarnine possesses only feebly basic properties, since its hydrochloride dissociates in the presence of water. It is readily soluble in alcohol, chloroform, or ether, but only sparingly so in hot water. It could not be converted by reduction into *iso*cotarnine, showing in this respect great similarity to oxycotarnine (Freund and Wulff, *Ber.*, 1902, **35**, 1737).

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CXXXVI.—*Monomethyl Laevulose and its Derivatives: Constitution of Laevulosediacetone.*

By James Colquhoun Irvine and Alexander Hynd, M.A. B.Sc. (Berry Scholar in Science).

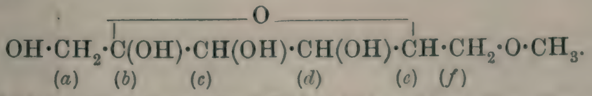
The application of the silver oxide method of alkylation to the formation of methylated ketoses has, so far, been confined to the preparation of tetramethyl lævulose and the corresponding alkylated methylfructosides. Purdie and Paul (Trans., 1907, **91**, 289), in the investigation referred to, encountered great experimental difficulties, but succeeded in examining the principal properties of crystalline tetramethyl lævulose and its derivatives. Past experience has shown that in work on alkylated sugars it is of the utmost importance to commence with a crystalline sugar derivative which can be obtained in one stereochemical form. Otherwise, particularly when the products are liquids, the whole series of reactions may have to be carried out with mixtures of α- and β-isomerides, and thus the values obtained for the rotatory powers have little significance.

In the case of lævulose, one of the few crystalline derivatives suitable for methylation is the α-lævulosediacetone discovered by Fischer. With the exception of acetonerhamnoside (Purdie and Young, Trans., 1906, **89**, 1196), the exact constitution of the condensation compounds of sugars with ketones is unknown, but it is evident that lævulosediacetone must contain one hydroxyl group, and the compound should therefore on methylation and hydrolysis be converted into monomethyl lævulose. The determination of the position of the methoxyl group in the alkylated ketose thus obtained would afford conclusive evidence of the structure of lævulosediacetone.

α-Methyl lævulosediacetone proved to be a crystalline solid, melting at 115°, and having $[\alpha]_D^{20}$ $-136{\cdot}4°$ in methyl-alcoholic solution. Although unaltered by prolonged boiling with water, the compound was easily hydrolysed by heating with 0·1 per cent. aqueous hydrogen chloride to give monomethyl lævulose. The latter substance possessed all the properties of a reducing sugar. It reduced Fehling's solution vigorously, and entered into ready condensation with either acetone or methyl alcohol, giving monomethyl lævulosediacetone and monomethyl methylfructoside respectively. When heated with phenylhydrazine acetate it gave a characteristic osazone, which was proved to be monomethylglucosazone. The sugar, moreover, was found to exist as α- and β-isomerides, the former being produced in the pure state by crystallisation from ethyl acetate, and the latter being formed in excess by fusion. As monomethyl lævulose is much less liable to undergo obscure decomposition changes than the unalkylated parent sugar, it is a convenient substance on which to study the mutarotation of ketoses. The results are given in detail in the experimental part.

When oxidised with bromine water, monomethyl lævulose gave, as the principal product, an acid, for which analytical figures were obtained agreeing with the calculated values for dihydroxymethoxybutyric acid. As after prolonged heating at 100° in a vacuum the analytical figures remained unaltered, and the titration figures still agreed for the free acid, we consider the compound to be incapable of forming a lactone.

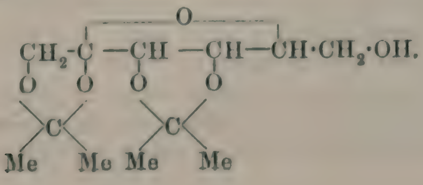
A review of all the above results affords complete evidence for the constitution of monomethyl lævulose, to which the following structure is ascribed:



$$\underset{(a)}{\mathrm{OH{\cdot}CH_2}}{\cdot}\underset{(b)}{\mathrm{C(OH)}}{\cdot}\underset{(c)}{\mathrm{CH(OH)}}{\cdot}\underset{(d)}{\mathrm{CH(OH)}}{\cdot}\underset{(e)}{\mathrm{CH}}{\cdot}\underset{(f)}{\mathrm{CH_2}}{\cdot}\mathrm{O{\cdot}CH_3}.$$

Considering the various possibilities, it is evident that the methoxyl group cannot be in positions (*a*) or (*b*), as it is present in the osazone formed from the sugar. Moreover, it cannot occupy position (*e*), as the compound is a reducing sugar and displays mutarotation. Of the three remaining alternatives, two are excluded by the fact mentioned above that the acid obtained from the sugar on oxidation also contains a methoxyl group and is incapable of forming a lactone. It follows from this that the alkyloxy-group must occupy the γ-position with reference to the carboxylic group, and this conclusion establishes the above structural formula.

Applying this result to the constitution of lævulosediacetone, it is seen that, if both acetone residues are similarly linked, two alternatives are possible, of which one may be reasonably excluded, as it involves the formation of two six-membered rings. The formula suggested for the substance is therefore:



Consideration of the optical activities of the various compounds described throws some light on the effect of methylation on the sugar molecule. It has hitherto proved impossible to obtain definite monosubstituted sugars other than the glucosides and the metallic derivatives, and thus the optical effect due to the successive substitution of the hydroxyl groups is unknown. In previous papers it has been pointed out that although the introduction of a new group into the glucosidic position results as a rule in marked changes in the rotatory power, the subsequent introduction of four methyl groups has comparatively little effect. In the case of lævulose complete methylation increases the activity in the lævo-sense, but it is here shown that the introduction of one methyl group into the terminal position lowers the lævorotation in a marked degree. This relationship holds whether we compare α-lævulose with monomethyl α-lævulose, the equilibrium mixtures of the sugars, or α-lævulosediacetone with monomethyl α-lævulosediacetone.

α-Lævulose	$[\alpha]_D^{20^\circ} = -104^\circ$	Diff. for one methyl group =33·5°.
Monomethyl α-lævulose	,, $= -70{\cdot}5^\circ$	
α-Lævulosediacetone	,, $= -150{\cdot}5^\circ$	Diff. for one methyl group =15·1°.
Monomethyl α-lævulosediacetone	,, $= -135{\cdot}4^\circ$	

On the other hand, comparing α-lævulose with tetramethyl α-lævulose, it is seen that the total effect of introducing the four methyl groups is to raise the lævorotation from −104° to −125°, so that methylation in position (*f*) diminishes the lævorotation by 33°, and the three methyl groups subsequently introduced increase the lævorotation by 54°. The total optical effect is therefore the additive sum of oppositely directed values, and this explains what has hitherto been regarded as an anomaly, namely, the relatively small changes in optical activity which result from complete substitution of the hydroxyl groups in sugars.

EXPERIMENTAL.

Preparation and Methylation of Lævulosediacetone.

The lævulosediacetone used in our experiments was prepared by Fischer's method (*Ber.*, 1895, **28**, 1164), and it was found that the success of the preparation varied considerably with the purity of the lævulose used; when the sugar was crisp enough to be well powdered and sifted through fine muslin, the subsequent condensation with acetone gave only relatively small amounts of syrupy by-products, and 50 per cent. yields of the desired product were obtained. On the other hand, some specimens of lævulose, although prepared from inulin and thoroughly dried in a vacuum before use, gave semi-crystalline, oily products, which were extremely difficult to purify. In all, 240 grams of lævulose were converted into the crystalline mixture of the α- and β-lævulosediacetones, the separation of which was effected by solution in dry ether and precipitation with light petroleum, or, more effectively, by crystallisation from the latter solvent. The melting point (117°) and the specific rotation ($[\alpha]_D^{20}$ $-162·8°$) of the main product agreed with the values quoted by Fischer for the pure α-form.

The methylation of the compound presented unusual difficulties, owing to the ready removal of the acetone residues by hydrolysis. The best results were obtained when not more than ten grams of lævulosediacetone were used in each experiment, special precautions being taken to exclude moisture during the process. The method is given in detail as an indication of how the alkylation reaction should be modified in the case of compounds which are easily hydrolysed.

Ten grams of α-lævulosediactone, dried at 100°, were dissolved at the boiling point in 16·5 grams of methyl iodide to which a little pure dry acetone had been added. The silver oxide used (13·5 grams) was dried at 95° until constant in weight, and was introduced as usual in small quantities at a time. The mixture was gently boiled for two hours, a glycerol-bath being substituted for a water-bath in order to avoid access of moisture from the outside of the condenser. Thereafter, 55 grams of methyl iodide and 45 grams of silver oxide were added in the usual manner, and the mixture boiled for a further period of six hours. The quantity of alkylating mixture used was largely in excess of the theoretical amount. The product was extracted by diluting largely with dry ether (free from acid) and boiling briskly for not more than fifteen minutes. The filtered liquid, after treatment with sodium sulphate, was evaporated to small bulk under the ordinary pressure, and concentrated to a syrup in a vacuum desiccator. Failure to observe any of the above directions resulted in the formation of acid syrups, which appeared to be mixtures of lævulose with oxidation products and methylated derivatives. When properly conducted, the syrup obtained was neutral in reaction, and crystallised readily in well-formed square plates mixed with a small quantity of unchanged lævulosediacetone, which was completely removed by treatment with water. The undissolved residue, after drying in a vacuum desiccator, was twice recrystallised from dilute methyl alcohol. Melting point, 115°; yield = 50 per cent.:

Found, C = 56·87; H = 8·15; OMe = 11·58.

$C_{12}H_{19}O_5·OMe$ requires C = 56·94; H = 8·03; OMe = 11·31 per cent.

As the molecular-weight determination by the cryoscopic method gave a normal result, the compound is evidently monomethyl α-lævulosediacetone. The substance dissolved readily in organic solvents generally, but was sparingly soluble in water. It behaved like a glucoside towards Fehling's solution, and was readily hydrolysed when heated with 0·1 per cent. aqueous hydrogen chloride. The following observations on the rotatory power of the compound were made:

Solvent :—	Acetone.	Methyl alcohol.	Benzene.
c.	2·6605	1·7040	1·7545
$[\alpha]_D^{20°}$	−135·3°	−136·4°	−149·4°

The effect of the different solvents on the rotatory power is similar to that observed with other alkylated sugar derivatives. The ease with which the acetone residues are removed is shown by the fact that the compound is completely converted into monomethyl methylfructoside when dissolved in methyl alcohol containing 0·25 per cent. of hydrogen chloride. Even at the temperature of the room, the specific rotation of the solution rapidly diminished, and after twenty-four hours action the liquid was practically inactive. Two days later the specific rotation, calculated on the quantitative conversion into the alkylated fructoside, was +11·1°, a result which agrees closely with the equilibrium value obtained for the pure compound. On working up the product in the usual manner, monomethyl methylfructoside was isolated in almost quantitative amount.

Monomethyl Laevulose.

As lævulose and its derivatives are readily decomposed by hydrogen chloride, the hydrolysis of monomethyl lævulosediacetone was carried out by means of very dilute acid. Thirty grams of the compound were dissolved in 525 c.c. of alcohol and diluted to 750 c.c. with water containing sufficient hydrogen chloride to make a 0·1 per cent. acid solution. After heating in boiling water for two hours, the rotation, which diminished steadily throughout the reaction, became constant. The final result obtained was $[\alpha]_D^{20}$ −26°, a value which approximates to that of monomethyl lævulose in similar concentration, so that apparently the hydrolysis is unaccompanied by any notable decomposition in the sugar molecule. The acid was removed by shaking with silver carbonate, and the filtered liquid heated with animal charcoal at 50° for an hour. After removal of the solvent by heating under diminished pressure, the residual syrup was extracted with warm alcohol. On evaporating the alcohol, a colourless syrup remained, which readily crystallised in diamond-shaped plates. After recrystallisation from ethyl acetate containing a little methyl alcohol, the compound melted at 122—123°:

Found, C = 43·28; H = 7·26; OMe = 15·59.

$C_6H_{11}O_5$·OMe requires C = 43·30; H = 7·22; OMe = 15·98 per cent.

Monomethyl lævulose is readily soluble in water or alcohol, but sparingly so in ordinary organic solvents. It reduces Fehling's solution vigorously on gentle warming, and gives the various colour tests described by Neuberg (*Zeitsch. physiol. Chem.*, 1900, **31**, 564). The fact that it gives a striking result with the Tollens' reagent is remarkable, as this test is supposed to be applicable to pentoses only. In the case of monomethyl lævulose, however, the hydroxyl content is the same as that of a pentose.

After heating the alkylated ketose for ten minutes with a slight excess of phenylhydrazine acetate, dissolved in dilute acetic acid, and cooling the solution, an abundant crop of delicate, yellow needles separated. After recrystallisation from dilute alcohol, the product melted at 142—144°, and analysis showed it to be monomethylglucosazone:

Found, $C = 61{\cdot}37$; $H = 6{\cdot}53$; $OMe = 8{\cdot}24$.

$C_{18}H_{21}O_3N_4{\cdot}OMe$ requires $C = 61{\cdot}30$; $H = 6{\cdot}45$; $OMe = 8{\cdot}34$ per cent.

The alkylated osazone proved to be much more soluble than glucosazone, and its formation serves as a delicate test for monomethyl lævulose.

Mutarotation of Monomethyl Laevulose.

After recrystallisation from ethyl acetate or from acetone, monomethyl lævulose behaves like α-lævulose, and displays mutarotation in the downward sense. For example, a 1 per cent. solution of the sugar in methyl alcohol gave initially ($l = 2$) a rotation of $-1{\cdot}75°$. This quickly diminished to the constant value $-0{\cdot}52°$, the same end-point being attained almost immediately by the addition of a trace of alkali. In aqueous solution the similar change was extremely rapid, and the rotation values differed considerably from those observed in alcoholic solution. As the sugar underwent no appreciable decomposition at the melting point, the effect of fusion in altering the proportion of the α- and β-forms was ascertained. After heating the pure α-form for a few minutes at a temperature slightly above the melting point, the product was quickly cooled, and the initial rotation determined without delay. As was expected, the reverse optical changes were then observed, the rotations increasing in the lævo-sense, indicating that an excess of the β-form had been produced. The results obtained with 1 per cent. solutions are summarised below:

Solvent.	Initial $[\alpha]_D^{20}$ of the α-form.		Permanent specific rotation.		Initial $[\alpha]_D^{20}$ of the fused sugar.
Water	$-70{\cdot}5°$	⟶	$-53{\cdot}1°$		
			$51{\cdot}1$	⟵	$-41{\cdot}9°$
Methyl alcohol	$74{\cdot}1$	⟶	$22{\cdot}1$		
			$21{\cdot}9$	⟵	$12{\cdot}5$

The different permanent values observed in aqueous and methyl-alcoholic solution are not due to the establishment of a different equilibrium in these solvents. This was shown by the following experiment: A solution of the sugar in methyl alcohol which had attained the permanent rotatory power ($-22{\cdot}1°$) was evaporated to dryness at the ordinary temperature under diminished pressure. The residue when dissolved in water showed no mutarotation, and gave at once the permanent value, $[\alpha]_D^{20}$ $-54{\cdot}0°$. A parallel experiment in which the equilibrium mixture was similarly recovered from aqueous solution and dissolved in methyl alcohol, showed the converse optical change, and no mutarotation was observed.

Oxidation of Monomethyl Lævulose.

Five grams of monomethyl lævulose were dissolved in water, and an aqueous solution of 10 grams of bromine added drop by drop, with constant stirring and thorough cooling. After eight hours' treatment, the liquid was shaken for one day, and the excess of bromine removed by heating under diminished pressure at 40°. The liquid was then largely diluted with water and distilled in a partial vacuum to half bulk, this process being repeated four times in order to remove hydrogen bromide and volatile acids. The undistilled residue was neutralised with silver carbonate, filtered, and decomposed with hydrogen sulphide. On evaporation of the filtrate in a partial vacuum, a syrup remained, which was extracted from traces of silver with methyl alcohol. On removal of the solvent, a clear acid syrup remained. The product was dried, first at 100° under the ordinary pressure, and finally at the same temperature under diminished pressure until constant in weight:

Found, $C = 39{\cdot}40$; $H = 6{\cdot}67$; $OMe = 18{\cdot}70$.
$C_4H_7O_4{\cdot}OMe$ requires $C = 39{\cdot}98$; $H = 6{\cdot}71$; $OMe = 20{\cdot}67$ per cent.

The analyses indicate that the compound is essentially $\alpha\beta$-dihydroxy-γ-methoxybutyric acid. 0·2404 Gram of the syrup, dried as before at 100° under 20 mm. pressure, required 14·9 c.c. $N/10$-barium hydroxide for neutralisation. After heating with 5 c.c. excess of the alkali, and titrating once more to the neutral point with hydrochloric acid, it was found that 3·01 c.c. of the baryta had been used. This result would be explained by the presence of about 6 per cent. of tartaric anhydride in the syrup, and, calculating on this assumption, the analytical figures are materially improved. In order to confirm the identity of the acid, it was converted into the barium salt, the usual method being followed to remove excess of barium hydroxide. By this process any barium tartrate formed would be left behind with the barium carbonate residues. The salt was obtained from the filtrate as a colourless, deliquescent glass:

Found, Ba = 32·2; theory requires Ba = 31·5 per cent.

Condensation Reactions of Monomethyl Laevulose.

When dissolved in acetone containing 0·2 per cent. of hydrogen chloride the sugar underwent ready condensation, and after a few hours the action on Fehling's solution disappeared. On working up the product as usual, a mixture of the stereoisomeric forms of monomethyl lævulosediacetone was obtained in excellent yield.

Monomethyl Methylfructoside.—On dissolving the sugar in twenty-five times its weight of methyl alcohol containing 0·22 per cent. of hydrogen chloride, a very rapid change in the rotation took place, and after a few minutes the solution was dextrorotatory. The reaction was completed by four hours heating at 40°, and during this treatment the rotation showed a marked rise and fall in the dextro-sense, indicating the formation of two stereoisomerides. After removal of the acid, treatment with animal charcoal, and evaporation of the solvent, the alkylated fructoside was obtained as a colourless syrup. Analysis of the compound dried at 100° in a vacuum gave:

C = 46·50; H = 7·77; OMe = 30·45.

$C_6H_{10}O_4(OMe)_2$ requires C = 46·12; H = 7·75; OMe = 30·03 per cent.

The preparation evidently consisted of a mixture of two forms, one of which is strongly dextrorotatory and the other feebly dextro- or possibly lævo-rotatory. The value found for the specific rotation in methyl-alcoholic solution was +11·3°. The compound was very readily hydrolysed, giving monomethyl lævulose, and when dissolved in a large excess of acetone containing a small proportion of hydrogen chloride, it was completely converted into monomethyl lævulosediacetone. The change in question therefore consisted in simultaneous hydrolysis and condensation, and emphasises the ready removal of groups from the fructosidic position.

Conversion into Tetramethyl Laevulose.—The alkylation of monomethyl methylfructoside by means of the silver oxide reaction proceeded normally in acetone solution, and, judging from the fact that the resulting oil was neutral in reaction and devoid of any action on Fehling's solution, the process was not accompanied by any hydrolysis or oxidation. After a second alkylation in methyl iodide solution, the product was recovered as usual, and distilled under diminished pressure. Analyses showed the syrup to be tetramethyl methylfructoside, and as the specific rotation in methyl alcohol was −18·9°, both the α- and β-forms were present.

The hydrolysis was carried out as described in the previous paper (*loc. cit.*), but more dilute acid (0·5 per cent.) was used. In this way decomposition of the alkylated ketose was probably avoided, as the syrupy product crystallised spontaneously without vacuum distillation. This method of obtaining tetramethyl lævulose through the intermediate formation of monomethyl methylfructoside possesses certain advantages over the alternative method of starting with methylfructoside. The latter compound cannot be obtained perfectly free from lævulose, and thus the alkylated products obtained from it are liable to contain oxidation acids, which are extremely troublesome to remove.

The general expenses of the above investigation were defrayed by a research grant from the Carnegie Trust, for which the authors desire to express their thanks.

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CXXXVII.—*Estimation of Iron by Permanganate in the Presence of Hydrogen Chloride.*

By John Albert Newton Friend, Ph.D.

Owing to the ease with which ferrous iron undergoes quantitative oxidation in contact with potassium permanganate, it is unfortunate that the reaction should yield inaccurate results in the presence of hydrogen chloride.

T. W. Harrison and F. M. Perkin (*Analyst*, 1908, **33**, 43) have shown that, even when the concentration of the hydrogen chloride is as low as $N/25$, the titrations are not accurate to within 2 per cent. W. Colet Birch (*Chem. News*, 1909, **99**, 61) has recently studied the modification detailed by Loewenthal and Lenssen (*Zeitsch. anal. Chem.*, 1861, **1**, 329) and Fresenius (*ibid.*, p. 361), but finds that it only gives approximate results.

It appeared to the present author, however, that the results obtained by different investigators did not agree sufficiently well amongst themselves, indicating that some constant source of error had been overlooked, and it was with the object of discovering this that the present research was undertaken.

Experiments were performed with $N/10$-solutions of both specially pure and commercial potassium permanganate, but the results were always the same. As the commercial salt is generally used in analytical practice, the results recorded in this paper are such as were obtained by using the latter solution, except where the contrary is stated. The ferrous iron solution was obtained by dissolving ferrous sulphate in water with the addition of just sufficient sulphuric acid to prevent the precipitation of basic salt. T. Warynski (*Ann. Chim. anal.*, 1909, **14**, 45) has shown that such solutions are very stable in contact with air. It was therefore unnecessary to use ferrous ammonium sulphate, as did Harrison and Perkin, and this is a decided advantage, since the presence of ammonium sulphate renders the titrations less accurate, as Birch has recently shown.

1. *Velocity of Titration.*

It was important to discover if the rate at which the permanganate is added to the ferrous solution affects the value of the titration. In each of the following three series the volumes titrated and the amounts of ferrous sulphate and hydrogen chloride were constant throughout, but the rapidity with which the titrations were effected was varied. A drop of manganese sulphate solution was added in each case before the titration was commenced.

Series I.		*Series II.*		*Series III.*	
50 c.c. $2m$*HCl. 5 c.c. $FeSO_4$.		50 c.c. mHCl. 5 c.c. $FeSO_4$.		50 c.c. $m/2$HCl. 5 c.c. $FeSO_4$.	
Time of titration. secs.	$KMnO_4$. c.c.	Time of titration, secs.	$KMnO_4$. c.c.	Time of titration, secs.	$KMnO_4$. c.c.
15	25·35	10	24·90	10	24·33
25	24·50	17	24·72	25	23·85
45	24·00	35	24·16	50	23·80
110	23·85	70	23·80	160	23·75
190	23·84	220	23·67	—	—
Theoretical value	23·52	Theoretical value	23·52	Theoretical value	23·52

* *m* signifies the molecular weight in grams per litre of solution.

The permanganate was run out of the burette at a uniform rate throughout each individual titration, and the flask was gently shaken all the time. The times of titration given above are therefore a direct measure of the shaking to which the ferrous sulphate solution was subjected.

Reference to the curve in which these results are given shows that:

(1) The error decreases as the time of titration increases, until the latter reaches about 100 seconds, after which the effect is negligible.*

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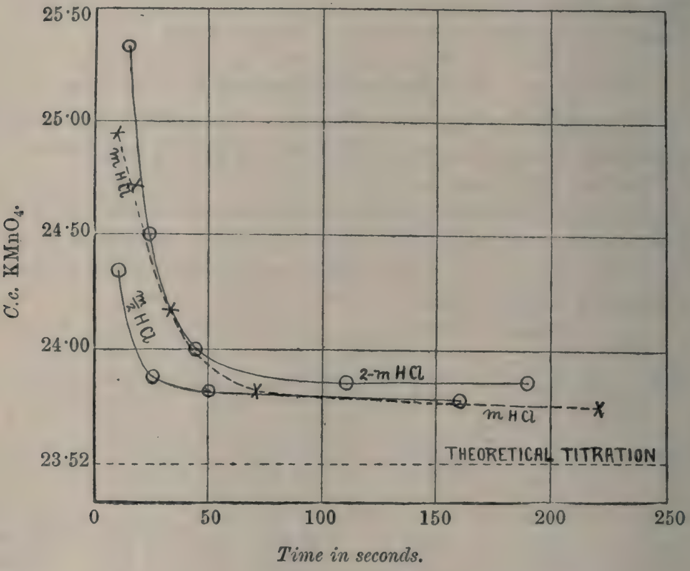
* Since the above was written, Mr. G. Cecil Jones, F.I.C., has kindly drawn my attention to the fact that Skrabal was, in 1903, aware of the fact that greater accuracy could be obtained by adding the permanganate slowly (*Zeitsch. anal. Chem.*, 1903, **42**, 373).

(2) The error increases with the concentration of the hydrogen chloride, but the difference is less marked when the time of titration exceeds 100 seconds.

It is clear, therefore, that if comparable results are to be obtained with different mixtures, the times of titration should not be less than about 100 seconds. The titrations recorded in the sequel have therefore been carried out with this velocity unless otherwise stated.

It was now necessary to determine if variation in the rate of addition of the first and last few c.c. of permanganate would appreciably affect the value of the titration. The results obtained are given in series IV.



Series IV.

A. 25 c.c. $2m$HCl. 5 c.c. $FeSO_4$.

	Commercial $KMnO_4$, c.c.	Error, c.c.
(1) The whole titration completed in 15 seconds	24·40	1·17
(2) 22 c.c. $KMnO_4$ added in 7 seconds and the titration completed slowly..	23·50	0·27
(3) Ditto, after an interval of 60 seconds	23·48	0·25
(4) Ditto, ,, ,, 300 ,, ...	23·48	0·25
(5) The whole titration effected slowly (100 seconds)	23·40	0·17
(6) Theoretical value	23·23	—

B. 50 c.c. *m*HCl. 25 c.c. $FeSO_4$.

	Pure $KMnO_4$, c.c.	Error, c.c.
(1) The whole titration completed in 15 seconds	24·40	1·60
(2) 21 c.c. $KMnO_4$ added in 7 seconds and the titration completed slowly	23·10	0·30
(3) Ditto, after an interval of 60 seconds	23·02	0·22
(4) Ditto, ,, ,, 300 seconds	23·05	0·25
(5) The whole titration effected slowly (100 seconds)	22·92	0·12
(6) Theoretical value	22·80	—

From the above it is clear that it is the rate at which the last few drops of permanganate are added to the ferrous solution which affects the value of the titration most. This is readily explained on the assumption that the reduction of the permanganate takes place in two stages. First, a partial reduction, resulting in the oxidation of some of the iron and the formation of an unstable perchloride of manganese. The latter substance now oxidises the ferrous iron according to the equation:

$$\mathrm{MnCl}_{(x+2)} + x\mathrm{FeCl}_2 \rightleftharpoons x\mathrm{FeCl}_3 + \mathrm{MnCl}_2$$

until equilibrium is established. If this latter reaction proceeds comparatively slowly, it is clear that when the last few drops of permanganate are added rapidly, excess must be taken before all the ferrous iron becomes oxidised and the usual pink colour indicative of the end-point can appear. On the other hand, prolongation of the time of titration beyond that required for equilibrium to be attained cannot affect the final result, as is well shown by titrations 2, 3, and 4 in series IV (A and B), and by the curve embodying the results of series I, II, and III. We may therefore hope to obtain accurate titrations in the presence of any substance which can cause equilibrium to be attained when the mass of the manganese perchloride is negligibly small, always provided that the rate of titration is sufficiently slow. As will be seen later, such a substance is manganous sulphate.

2. *The Effect of Dilution.*

As is evident from the results given in series V and VI, dilution slightly increases the error of titration. The end-point, however, becomes clearer, which is a decided advantage when working by gaslight.

Series V.

25 c.c. *m*HCl. 5 c.c. $FeSO_4$.

Total volume titrated, c.c.	Water, c.c.	$KMnO_4$, c.c.
30	0	23·73
80	50	23·78
130	100	23·90
180	150	23·98
	Theoretical value	23·52

Series VI.

10 c.c. 2*m*HCl. 5 c.c. $FeSO_4$.

Total volume titrated, c.c.	Water, c.c.	$KMnO_4$, c.c.
15	0	23·70
65	50	23·75
115	100	23·78
165	150	23·82
	Theoretical value	23·48

These results are in agreement with those obtained by Birch (*loc. cit.*) under different conditions.

3. *Action of Sulphuric Acid.*

The results given in series VII show that the presence of small quantities of sulphuric acid tends to decrease the error of titration. This is in harmony with the results obtained by Skrabal, Kessler, and others. When present in large excess, however, the action of the acid appears to be less favourable.

Series VII.

A. *With Commercial* $KMnO_4$.

Total volume titrated, c.c.	Conc. of HCl.	Conc. of H_2SO_4.	Titre in c.c. $KMnO_4$.	Correct titre, c.c.	Error, c.c.
65	*m*/3	—	23·80	23·48	0·32
65	*m*/3	3*m*	23·75	23·48	0·27
115	*m*/6	—	23·80	23·48	0·32
115	*m*/6	4*m*	23·90	23·48	0·42
80	*m*/3	—	23·25	23·00	0·25
80	*m*/3	2·5*m*	23·25	23·00	0·25
130	*m*/5	—	23·33	23·00	0·33
130	*m*/5	3*m*	23·52	23·00	0·52

B. *With Pure* $KMnO_4$.

Total volume titrated, c.c.	Conc. of HCl.	Conc. of H_2SO_4.	Titre in c.c. $KMnO_4$.	Correct titre, c.c.	Error, c.c.
125	*m*/2·5	—	23·16	22·45	0·71
125	*m*/2·5	1·6*m*	23·12	22·45	0·67
225	*m*/4·5	—	23·23	22·45	0·78
225	*m*/4·5	1·8*m*	23·16	22·45	0·71
325	*m*/6·5	—	23·30	22·45	0·85
325	*m*/6·5	2·5*m*	23·38	22·45	0·93

4. *Effect of Age of Permanganate Solution.*

The permanganate solution was prepared by dissolving the requisite amount of ordinary potassium permanganate in cold water, as is usual in works. The solution was kept in a glass-stoppered bottle exposed to the diffused light of the laboratory. If it had been pure it would have remained unaltered for many months, as has been shown by Gardner and North (*J. Soc. Chem. Ind.*, 1904, **23**, 599), and more recently by Collitt (*Pharm. J.*, 1908, **27**, 724). The present author observed some years ago, however, that permanganate which had not been specially purified gave uncertain results in certain cases after keeping for two or three days (Trans., 1905, **87**, 1369). It was important, therefore, to discover if the reaction under consideration is affected by the age of the permanganate solution, as it is inconvenient to make up a fresh one every time a titration is to be made.

In series VIII and IX are given the results of titrating 5 c.c. of ferrous sulphate solution with fresh and old permanganate solutions respectively in the presence of varying quantities of hydrogen-chloride.

Series VIII.

HCl, c.c.	$KMnO_4$ (fresh), c.c.	Error c.c.
0	23·48	0·00
10 (2*m*)	23·70	0·22
25 (2*m*)	23·90	0·42
50 (*m*)	23·90	0·42
50 (2*m*)	23·93	0·45

Series IX.

HCl, c.c.	$KMnO_4$ (7 days old), c.c.	Error, c.c.
0	23·23	0·00
10 (2*m*)	23·48	0·25
25 (2*m*)	23·54	0·31
50 (*m*)	23·50	0·27
50 (2*m*)	23·70	0·47

From the above results it is clear that if the permanganate is kept free from organic matter there is little to choose between a fresh solution and one several days old.

5. *Action of Manganous Sulphate.*

Attention has been repeatedly called to the fact that addition of manganous sulphate to the ferrous salt to be titrated in the presence of hydrogen chloride decreases the error considerably (see Kessler, *Zeitsch. anal. Chem.*, 1863, **1**, 329; Zimmerman, *Ber.*, 1881, **14**, 779; Hauffe, *Chem. Zeit.*, 1897, **21**, 894; Willenz, *Chem. Zentr.*, 1899, i, 638; Baxter and Frevert, *Amer. Chem. J.*, 1905, **34**, 109; Harrison and Perkin, *loc. cit.*; Birch, *loc. cit.*). Opinion, however, seems to be divided as to the amount of the salt which should be taken. Treadwell (*Anal. Chem.*, 1st Ed., ii, 483) suggests that the amount should not exceed that of the iron salt in solution. On the other hand, A. Müller (*Stahl u. Eisen*, 1906, **26**, 1477) employs larger quantities. Harrison and Perkin state that variation in the amount of manganous sulphate does not affect the titration materially when not less than one gram is taken. Their own results, however, do not seem to justify this statement (*loc. cit.*, p. 44), and by a curious oversight, neither the concentration of the iron solution nor that of the permanganate is given.*

The great difficulty experienced in titrating solutions containing considerable quantities of manganous sulphate is that of determining the end-point, for in concentrated solution, in the presence of hydrogen chloride, the usual pink tint caused by the permanganate is apt to be fugitive, producing a brown coloration. This may be avoided by diluting largely, but, as is shown above, dilution tends to increase the error.

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* In a private communication Dr. Perkin has kindly informed me that he used *N*/10-permanganate solution.

In series X are given the results of experiments performed in order to determine the effect of increasing the concentration of the manganous sulphate. The salt used was analysed, found to be free from iron, and to be correctly represented by the formula $MnSO_4,4H_2O$.

Series X.

Total volume titrated, 65 c.c. Conc. of HCl, *m*/3.

Weight of $MnSO_4,4H_2O$. grams.	$KMnO_4$. c.c.	Error, c.c.	Remarks.
0·0	23·75	0·27	End point clear
0·1	23·60	0·12	,, ,,
0·25	23·60	0·12	,, ,,
0·5	23·52	0·04	,, ,,
1·0	23·50	0·02	,, ,,
2·0	23·48	0·00	Fugitive end point
3·0	23·48	0·00	End point momentary
5·0	—	—	No clear end point

Theoretical value = 23·48 c.c.

These results show that when not less than one gram of manganese sulphate is present the titrations under the special conditions of the above experiments are accurate.

6. *Correct Titrations.*

It is clear from the above that we may expect to obtain accurate estimations of ferrous iron by titration with potassium permanganate in the presence of hydrogen chloride provided that:

1. The titration is effected slowly and with constant shaking.
2. A sufficient quantity of manganous sulphate is present.
3. The volume of the ferrous solution is sufficiently large to ensure a good end-point, but not so great as to reduce the accuracy of the titration.

That our expectations may be realised is shown by the results detailed in series XI.

Series XI.

Total volume titrated, 200 c.c.

Weight of $MnSO_4,4H_2O$. grams.	Conc. of HCl.	$KMnO_4$ required, c.c.	Theoretical value, c.c.	Error, c.c.
3·0	*m*/4	27·50	27·47	0·03
2·0	*m*/4	25·38	25·34	0·04
2·0	*m*/4	25·36	25·32	0·04
3·0	*m*/5	27·50	27·47	0·03
2·0	*m*/5	25·38	25·34	0·04
3·0	*m*/8	27·48	27·47	0·01
2·0	*m*/8	25·40	25·34	0·06

In order to ensure thorough mixing of the permanganate with the ferrous solution, the orifice of the burette was made smaller, so that thirty seconds were required to deliver 30 c.c. of liquid when the tap was full on. The permanganate was added at such a rate that the individual drops could be distinguished as they fell, and the ferrous solution was well shaken all the time. As the end point was approached, the permanganate was added very slowly, the colour of each drop disappearing before the next drop was added. There was no odour of chlorine perceptible at the end of the titrations.

It will be evident that, when the above precautions are rigidly observed, fairly accurate estimations of ferrous iron may be made in the presence of any concentration of hydrogen chloride not exceeding $m/4$ by titration with $N/10$ potassium permanganate, provided the volume titrated does not exceed 200 c.c. and the weight of manganous sulphate is not less than 2 grams. The results were found to be slightly less accurate if the concentration of the hydrogen chloride exceeded $m/4$ and the weight of manganous sulphate was appreciably less than 2 grams. The results given above agree well within the usual range of experimental error. The end-points were just as well defined as when the pure permanganate solution was employed.

The research is being continued with the object of determining the most suitable concentrations of permanganate and manganous sulphate for the estimation of varying quantities of ferrous salts under different conditions of acidity.

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CXXXVIII.—*The Action of Sulphur Monochloride on Salts of Organic Acids: a Convenient Method of Preparing Anhydrides.*

By WILLIAM SMITH DENHAM.

HEINTZ (*Jahresber. Chem.*, 1856, 569) investigated the action of sulphur dichloride, SCl_2 ("chlorschwefel," SCl, in the old notation), on anhydrous salts of organic acids, and found that the reaction always takes place so that a metallic chloride and sulphate are formed and sulphur separates. He proposed a method for the preparation of benzoic anhydride based on the reaction between dry sodium benzoate and sulphur dichloride, benzoyl chloride being first formed according to the equation:

$$4C_6H_5\cdot CO_2Na + 3SCl_2 = 2S + Na_2SO_4 + 2NaCl + 4C_6H_5\cdot COCl,$$

this reacting at 150° with excess of sodium benzoate to give benzoic anhydride. Heintz used no solvent for the sulphur dichloride.

The author has found that the sodium, or better, the silver, salts of many monobasic organic acids react smoothly with sulphur monochloride in presence of such solvents as light petroleum, ether, or benzene to give the chloride of the metal and unstable derivatives of the acids, in which, apparently, sulphur replaces the hydrogen of the hydroxyl group. These compounds decompose even when kept in sealed tubes, and the products of decomposition are found to be the anhydride of the acid, sulphur dioxide, and free sulphur. The following equations may perhaps be taken as representing respectively the formation and decomposition of the benzoic acid derivative:

$$2C_6H_5\cdot CO_2Na + Cl_2S_2 = (C_6H_5\cdot CO_2S)_2 + 2NaCl.$$
$$2(C_6H_5\cdot CO_2S)_2 = 2(C_6H_5\cdot CO)_2O + SO_2 + 3S.$$

Similar unstable derivatives have been obtained from *o*-toluic, *m*-toluic, *p*-toluic, acetic, phenylacetic, and propionic acids. Those from *m*- and *p*-toluic acids are apparently the most stable. The ready formation and simple decomposition of these compounds (both reactions appear to be quantitative) afford a convenient and rapid method of preparing the anhydrides of the acids.

It was thought to be possible that more stable compounds of the same kind might be obtained from derivatives of the above acids. So far, the silver salts of salicylic, ethylsalicylic, and *o*-nitrobenzoic acids only have been examined, and it has been found that, although reactions take place between these salts and sulphur chloride, they are apparently more complex.

Among dibasic acids, oxalic, malonic, succinic, and the three phthalic acids have been studied. Of these, only the salts of succinic and phthalic acids appear to react at all readily, but no intermediate compounds have been obtained, the anhydrides alone being formed.

Metallic derivatives of imides, for example, potassium phthalimide, react with sulphur chloride. A stable compound, $C_6H_4(CO)_2NS$, has been obtained in this way, and the same compound can be prepared by the action of sulphur chloride on phthalimide in presence of pyridine.

The investigation of the action of sulphur monochloride on metallic salts and on compounds containing imino-groups is being continued.

EXPERIMENTAL.

Action of Sulphur Monochloride on Sodium Benzoate.—This reaction has been carried out repeatedly in slightly varying ways, using different solvents; the following may be taken as typical. 2·9 Grams of dry, powdered sodium benzoate were mixed with about 20 c.c. of light petroleum, and the calculated quantity (1·4 grams) of sulphur chloride dissolved in a few c.c. of the same solvent was added all at once. The mixture was then boiled on the water-bath for a hour and a-half under a reflux condenser provided with a calcium chloride tube; a slight odour of sulphur dioxide was noticed during this operation. About one gram of freshly reduced copper powder * was then added, and the boiling was continued for half-an-hour longer. The copper became black, and the solution green, but, on filtering, a clear, colourless liquid was obtained, from which crystals separated on cooling. In this way a good yield is obtained of the substance, $(Ph\cdot CO_2S)_2$, in well-defined, colourless crystals, which, however, soon turn yellow and evolve sulphur dioxide, leaving sulphur and benzoic anhydride. This decomposition takes place even in an atmosphere of carbon dioxide, and in warm weather may occur instantaneously with the formation of a liquid mass consisting of a mixture of sulphur and benzoic anhydride. The compound is easily soluble in alcohol, ether, benzene, carbon disulphide, or glacial acetic acid, more sparingly so in light petroleum. The solution in benzene may be kept for a day or two without evidence of decomposition, whilst that in glacial acetic acid soon decomposes. The substance, when dissolved in petroleum, reacts with ammonia, but no definite product other than ammonium benzoate could be obtained. It reacts also with aniline.

The sulphur was estimated in some of the freshly prepared and recrystallised substance, which had been quickly dried by warming it gently in a current of carbon dioxide:

0·5098 gave 0·7928 $BaSO_4$. S = 21·32.

0·39 in 13·09 benzene gave $\Delta t = -0{\cdot}53$. M.W. = 281.

$C_{14}H_{10}O_4S_2$ requires S = 20·92 per cent. M.W. = 306.

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* The copper is not essential. It was added in one experiment to see if it would remove the sulphur and leave benzoyl peroxide, but this did not happen. The use of it was continued in after experiments, since it appeared to destroy final traces of sulphur chloride and to be better for this purpose than excess of sodium benzoate.

This compound, $(C_6H_5\cdot CO_2S)_2$, may be prepared more readily by shaking together dry silver benzoate and a solution of sulphur chloride in ether in the manner described below for other silver salts.

Action of Sulphur Monochloride on Silver Acetate.—Since sulphur chloride does not react readily with sodium acetate, the silver salt was employed, and after a number of preliminary experiments, the following simple method was found to give satisfactory results.

To 2·5 grams of dry silver acetate, about 20 c.c. of dry ether were added, and then 0·4 c.c. (rather less than the calculated quantity) of sulphur chloride, dissolved in a few c.c. of dry ether. The containing vessel was closed and shaken for a minute, when the mixture became warm and the yellow colour of the sulphur chloride disappeared.

After filtering, the ether was distilled off, the last traces being removed by means of a current of dry hydrogen. The compound, $(CH_3\cdot CO_2S)_2$, was thus obtained as a clear, faintly yellow, viscous liquid with a faintly pungent odour. Some of it, after being kept for three days in a closed flask in the ice-chest, was found to be completely decomposed into sulphur dioxide, sulphur, and acetic anhydride:

0·6248 gave 1·5984 $BaSO_4$. S = 35·14.
0·617 in 19·94 benzene gave $\Delta t = -0{\cdot}895$. M.W. = 173.
$C_4H_6O_4S_2$ requires S = 35·16 per cent. M.W. = 182.

Action of Sulphur Monochloride on Silver Propionate.—This experiment was carried out exactly as was the one with silver acetate, and a compound, $(C_2H_5\cdot CO_2S)_2$, was obtained, of which the properties were exactly similar to those of the compound derived from acetic acid, and decomposed similarly:

0·6910 gave 1·5436 $BaSO_4$. S = 30·68.
0·998 in 16·19 benzene gave $\Delta t = -1{\cdot}59$. M.W. = 194.
$C_6H_{10}O_4S_2$ requires S = 30·48 per cent. M.W. = 210.

Preparation of Propionic Anhydride from Silver Propionate.—To 18·1 grams of dry silver propionate in about 50 c.c. of dry ether, 4 c.c. of sulphur chloride in 20 c.c. of dry ether were added; this addition must be made gradually, as otherwise the reaction may become too vigorous. The mixture was then shaken for a minute, and after filtering off the silver chloride and removing the ether by distillation, the syrup obtained was heated on the water-bath for an hour or two until decomposition was complete. The clear liquid was then decanted and distilled, the distillation being stopped as soon as the distillate appeared yellow; 5·5 grams of the crude anhydride distilled between 160° and 170°, the greater portion above 165°. The boiling point of propionic anhydride is 168°, and the calculated yield from 18·1 grams of silver propionate is 6·5 grams.

Preparation of Propionic Anhydride from Sodium Propionate.—9·6 Grams of dry sodium propionate were boiled for an hour under reflux with 4 c.c. of sulphur chloride in presence of 40 c.c. of light petroleum, a little copper powder being added towards the end. The solution was then filtered from sodium chloride and treated as just described in the preparation from the silver salt; 4·5 grams of the crude anhydride distilled over at a little below 170°. The theoretical yield is 6·5 grams.

Action of Sulphur Monochloride on Silver Phenylacetate.—This reaction was carried out exactly in the way described in the case of silver acetate, a slight excess of the silver salt being used. The compound, $(C_6H_5\cdot CH_2\cdot CO_2S)_2$, was obtained as a pale yellow, very viscous liquid with a faint odour, which partly crystallised when cooled in ice. If heated in the steam-oven, it decomposes in a few minutes, and when kept in a sealed tube, decomposition is apparent in two days. The only products of decomposition observed were sulphur dioxide, sulphur, and phenylacetic anhydride. The last-named substance can readily be purified by recrystallisation from benzene with addition of light petroleum. It was identified by a determination of its melting point and by conversion into phenylacetic acid:

0·2826 gave 0·3930 $BaSO_4$. S = 19·10.
0·795 in 16·95 benzene gave $\Delta t = -0·78$. M.W. = 301.
$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

Action of Sulphur Monochloride on Silver o-*Toluate.*—This reaction was carried out much as described in the case of silver acetate, but as the product is a crystalline solid, it was precipitated by distilling off most of the ether, then adding light petroleum, and cooling in ice. The compound, $(C_6H_4Me\cdot CO_2S)_2$, is a white, crystalline, odourless solid, which decomposes in two or three hours. It resembles the benzoic acid derivative in being more stable in solution in benzene than in the solid state. The decomposition products were sulphur, sulphur dioxide, and *o*-toluic anhydride, which was identified by a determination of its melting point and by conversion into *o*-toluic acid:

0·3538 gave 0·5120 $BaSO_4$. S = 19·82.
0·567 in 18·17 benzene gave $\Delta t = -0·53$. M.W. = 294.
$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

Action of Sulphur Monochloride on Silver m-*Toluate.*—The experiment was carried out exactly as in the case of silver acetate. The compound, $(C_6H_4Me\cdot CO_2S)_2$, was a very viscous, slightly yellow, but perfectly transparent syrup, with almost no odour. It is apparently more stable than any of the foregoing compounds. When kept in a sealed tube it slowly crystallised, and the crystalline mass appeared to be largely undecomposed a week after preparation. When examined ten days after preparation, the appearance of the tube indicated that the substance had decomposed suddenly:

0·3192 gave 0·4414 $BaSO_4$. S = 18·99.

0·488 in 23·35 benzene gave $\Delta t = -0{\cdot}38$. M.W. = 275.

$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

The decomposition products were sulphur, sulphur dioxide, and *m*-toluic anhydride. The latter was dissolved in sodium hydroxide solution, and on acidifying the solution, *m*-toluic acid was precipitated. *m*-Toluic anhydride does not seem to have previously been prepared:

0·1816 gave 0·5008 CO_2 and 0·0952 H_2O. C = 75·21; H = 5·82.

$C_{16}H_{14}O_3$ requires C = 75·59; H = 5·51 per cent.

m-*Toluic anhydride* melts at 71° and boils about 230°/17 mm. It is very soluble in ether, benzene, chloroform, or other solvents, but may readily be crystallised from light petroleum. It is not readily attacked by water or by sodium hydroxide solution. It is easily prepared by the following method. Two c.c. of sulphur chloride in 20 c.c. of dry ether were added to 12·5 grams of dry silver *m*-toluate (instead of 12·15 grams) in 50 c.c. of ether. After shaking, filtering, and removing the ether by distillation, the sulphur compound was heated on the water-bath until sudden decomposition set in, and when decomposition was complete, the anhydride was extracted with ether. A nearly theoretical yield was obtained of the crude anhydride, which may be purified by recrystallisation from light petroleum, making use of animal charcoal.

The formation and decomposition of the compound $(C_6H_4Me{\cdot}CO_2S)_2$ were followed quantitatively, with the following results: 12·15 grams of silver *m*-toluate gave 7·7 grams of the compound $(C_6H_4Me{\cdot}CO_2S)_2$ instead of the calculated yield, 8·3 grams; 7·7 grams of the compound $(C_6H_4Me{\cdot}CO_2S)_2$ gave 0·88 gram of sulphur dioxide,* 5·9 grams of crude anhydride (containing a little sulphur), and 0·87 gram of sulphur. According to the equation $2(C_6H_4Me{\cdot}CO_2S)_2 = 2(C_6H_4Me{\cdot}CO)_2O + SO_2 + 3S$, 7·7 grams of the substance should yield 0·74 gram of sulphur dioxide, 5·7 grams of anhydride, and 1·1 grams of sulphur.

Action of Sulphur Monochloride on Silver p-*Toluate.*—The reaction was carried out as before. The compound, $(C_6H_4{\cdot}Me{\cdot}CO_2S)_2$, begins to crystallise while the ether is being distilled off. It is a white, crystalline solid:

0·2604 gave 0·3766 $BaSO_4$. S = 19·87.

0·436 in 13·99 benzene gave $\Delta t = -0{\cdot}50$. M.W. = 312.

$C_{16}H_{14}O_4S_2$ requires S = 19·16 per cent. M.W. = 334.

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* Determined by the loss of weight after evolution of the sulphur dioxide.

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